Development of Molecular Glasses for Solvent-Free Photolithography utilizing Combinatorial Vapor Deposition

Dissertation

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dedicated to my family

„Unser Leben ist das, wozu es unser Denken macht.“

Marcus Aurelius

(121-180)

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ABBREVIATIONS

CAR	chemically amplified resist
CVD	chemical vapor deposition
DMAP	dimethyl aminopyridine
DNQ	diazonaphthoquinone
DSC	differential scanning calorimetry
DUV	deep ultraviolet
DRAM	dynamic random access memory
E_0	dose to clear
EA	elemental analysis
EDAC	1-(3-dimethylaminopropyl-)-3-ethylcarbodiimide hydrochloride
e.g.	*exempli gratia* (for example)
EUV	extreme ultraviolet
excimer	excited dimer
HPLC	high pressure liquid chromatography
HRMS	high resolution mass spectrometry
ICs	integrated circuits
i.e.	*id est* (that is)
IR	infrared
LMR	low molecular weight resist
NMR	nuclear magnetic resonance
OFET	organic field-effect transistor
OLED	organic light emission device
PAB	post application bake
PAG	photo acid generator
PEB	post exposure bake
PGMEA	propylene glycol methyl ether acetate
PVD	physical vapor deposition
SEM	scanning electron microscopy
rpm	revolutions per minute
T_b	boiling temperature
t-BOC	*tert*-butyloxycarbonyl

T_c	crystallization temperature
T_g	glass transition temperature
TGA	thermogravimetric analysis
THF	tetrahydrofuran
T_m	melting point
T_{rc}	recrystallization temperature
TMAH	tetramethylammonium hydroxide
triflate	trifluoromethanesulfonate
UV	ultraviolet
VDP	vapor deposition polymerization

TABLE OF CONTENTS

1. INTRODUCTION

1.1 Lithography

1.1.1 History and current state of lithography

Lithography is the process of producing patterns on a substrate by irradiation. The name derives from the Greek words “lithos” which means “stone” and “graphein” which means “to write”. In the 19th century, it was a usual way for printing articles, and additionally it became an art direction. Some decades later, the term was introduced to semiconductor industry. Even though it has been already seriously investigated since the 1930s, it is an unbowed research field. For financial reasons, the main goal of lithography research targets a decrease in pattern size and performance improve. Over time, the exposure wavelength became a limiting factor of photolithographic processes. Thus, not only new materials were investigated, but also new process techniques were established. Additionally, there are several general requirements of lithography materials.[1] Among others, those are sensitivity, contrast, etching resistance, purity, line edge roughness, and environmental issues.

The first industrial photoresist system was poly(vinyl alcohol) containing cinnamic components in the side chains. When exposed to light, a [2+2] cycloaddition took place, and a network of crosslinked polymer chains formed. This resist was employed in photographic processes since the 1930s.

35 years ago, when integrated circuits (ICs) were initially produced, azido/isoprene resists were exposed to ultraviolet (UV) broadband spectrum, providing resolutions only larger than 2 µm. These structures were used for chips from 1 to 16 kBit DRAM. When the need for faster chips evolved, the chemistry of the photolithography process changed. Positive resists based on a mixture of Diazonaphthoquinone (DNQ) and Novolak (a condensation product of phenol and formaldehyde) were employed for G-line (436 nm) and I-line (365 nm) steppers. I, G and H lines are the typical distinct lines of mercury-vapor lamps which are the standard light sources in photolithography. The new resist was useful for chips up to 64 MBit DRAM. Structures sizes of 0.25 µm could be reproducibly manufactured by employing special

exposure equipment like series of lenses which condense the image of the mask to project it onto the photoresist. This resolution seems to be the limit for I line lithography.

Nowadays, asking for process performance up to 4 GBit DRAM (Fig. 1-1), chemically amplified resists (CARs) like polyhydroxystyrene-based polymers in combination with a photoacid generator (PAG) are in use. They are exposed to deep ultraviolet (DUV) irradiation (248 and 193 nm).[2] These small wavelengths are generated by excited dimer ("excimer") lasers. This term is used for lasers which, under suitable conditions, produce UV light which is well-focused and can be precisely controlled. Lithography based upon excimer lasers of argon fluoride ArF, combined with new techniques like immersion lithography in which a liquid with a refractive index greater than 1 replaces the air gap between mask and optics, allows at present time linewidths of 32 nm.[3] Lenses are made of special material, e.g. calcium fluoride CaF_2. Mechanical problems like reflection or material damage have to be controlled by the improvement of these apparatuses.[4]

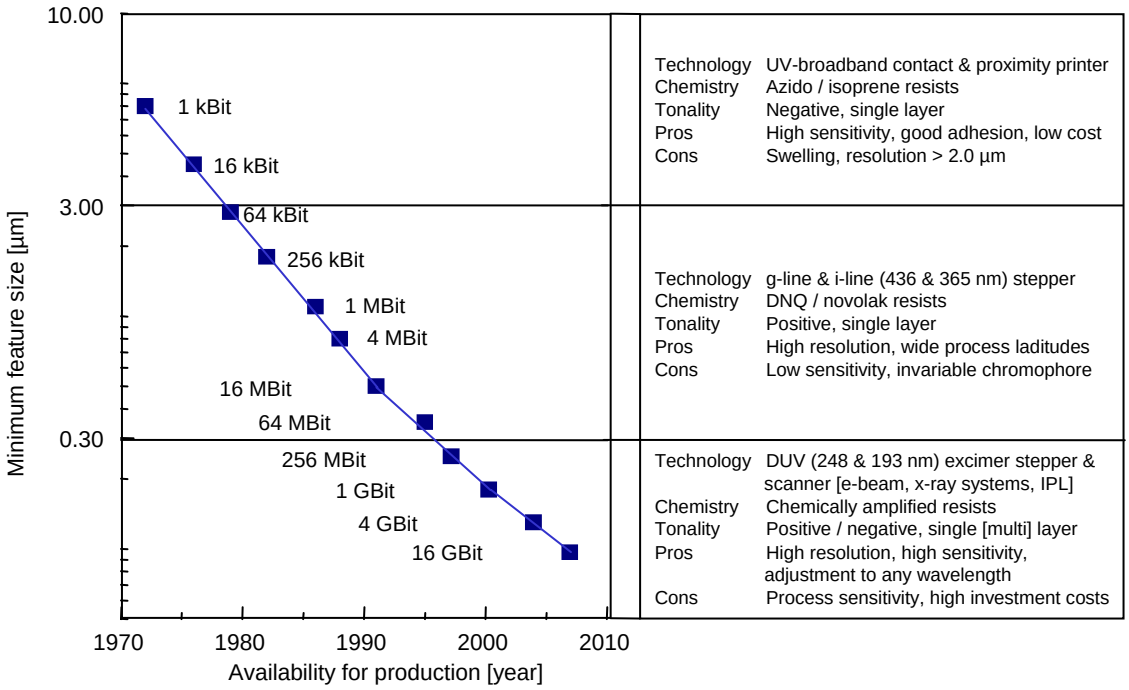


Figure 1-1. Development of storage capacity and minimum feature size of memory devices (left) and technologies usable for memory device production (right).[4]

Even though the resolution problems are evident and diffraction limits the possibilities of optical lithography, this method is still considered to be the most suitable for standard processes. It is established, relatively cheap, and very fast compared to other methods. The less time consuming procedure is due to the fact that via photolithography, patterns can be formed parallel. By other methods which are able to produce sub-100 nm patterns such as electron beam, the structures are usually created successively since they are directly written

into the resist.[5] There are endeavors to establish parallel writing e-beam systems which might become an alternative with respect to resolution and throughput in future.[6] Additionally, investigations towards alternative techniques are performed. X-ray lithography suffered in the beginning from difficult mask fabrication and repair since the required accuracy is higher than for those in optical systems, but issues of deformation of the thin membrane material[7] has been overcome in the last years.[8] Lithography based upon extreme ultraviolet (EUV) in the range of 11 to 14 nm, also called soft x-ray, is another field of interest. Since all materials, even air, absorbs EUV light, the patterning has to performed in vacuum. Other research issues include suitable materials for multilayer reflectors and light sources.[7]

The results of the continuous development and improvement in lithography are proving the so-called Moore's law. In 1965, Intel founding member Gordon E. Moore predicted that innovations in technology would allow a doubling of the number of transistors in a given space every time period which he later specified to 18 to 24 months.[9] He also stated that manufacturing costs would dramatically drop and speed would significantly increase as technology advances. Forty years later, this forecast is still proven to be true (see Fig. 1-2).

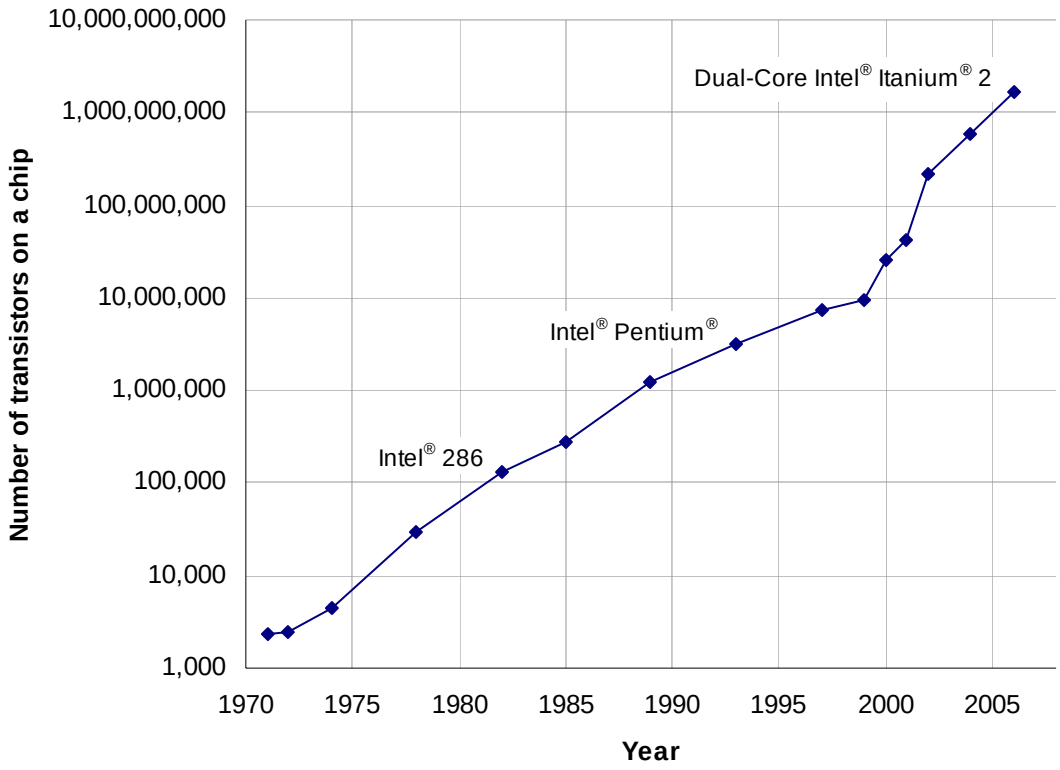


Figure 1-2. The doubling amount of transistors on a chip every 18 to 24 months proves Moore's law which was set up in 1965 (data according to [10]).

Besides resolution, several other parameters are important for the performance of a photoresist. For example, the term “sensitivity” characterizes the necessary energy dose for a resist to react sufficiently. To determine this dose for a positive resist (see Ch. 1.1.2), the resist solution is coated onto a substrate, heated to remove the solvent, exposed to different exposure doses, and developed. By measuring the remaining film thicknesses,[11] the amount of exposure energy at a certain wavelength that is necessary to just clear the resist in a large area for a given process is determined.[12] This “dose to clear” (E_0) or “clearing dose” defines the sensitivity of a resist and is an important time and thus cost factor. For resolutions in the range of 100 nm and smaller, another important parameter is line edge roughness (LER) which can represent a significant fraction of the linewidth,[7] particularly in very small features.

1.1.2 General principles

The requirements towards more stable systems and increasing resolution still advances the search for new or improved substances, methods and techniques. The basic principle of lithography is the change of physical properties, e.g. solubility, of one or various mixture components by irradiation. A chemical system which can be changed in that way is called “resist”. This term is derived from resistant and is generally used for a material that is applied on areas of a substrate surface to protect them from the reagent in question during chemical or physical treatment.[13] When only partly exposed to radiation, the generated difference in the physical properties can be exploited to easily remove one part of the resist–either the exposed or the unexposed part. By doing so, small patterns even in the nanometer range can be created, provided that the applied techniques facilitate this resolution.

Lithography which uses light as irradiation source is specified as photolithography or optical lithography. The wavelength of irradiation became a limiting factor of creating patterns, thus it is often applied in the range of UV or DUV. Patterns are produced by exposing the resist through a mask. Because of this fast feature production, photolithography is favored for series production.

The photolithography process to produce the desired patterns can be roughly divided into three steps which are illustrated in Figure 1-3.

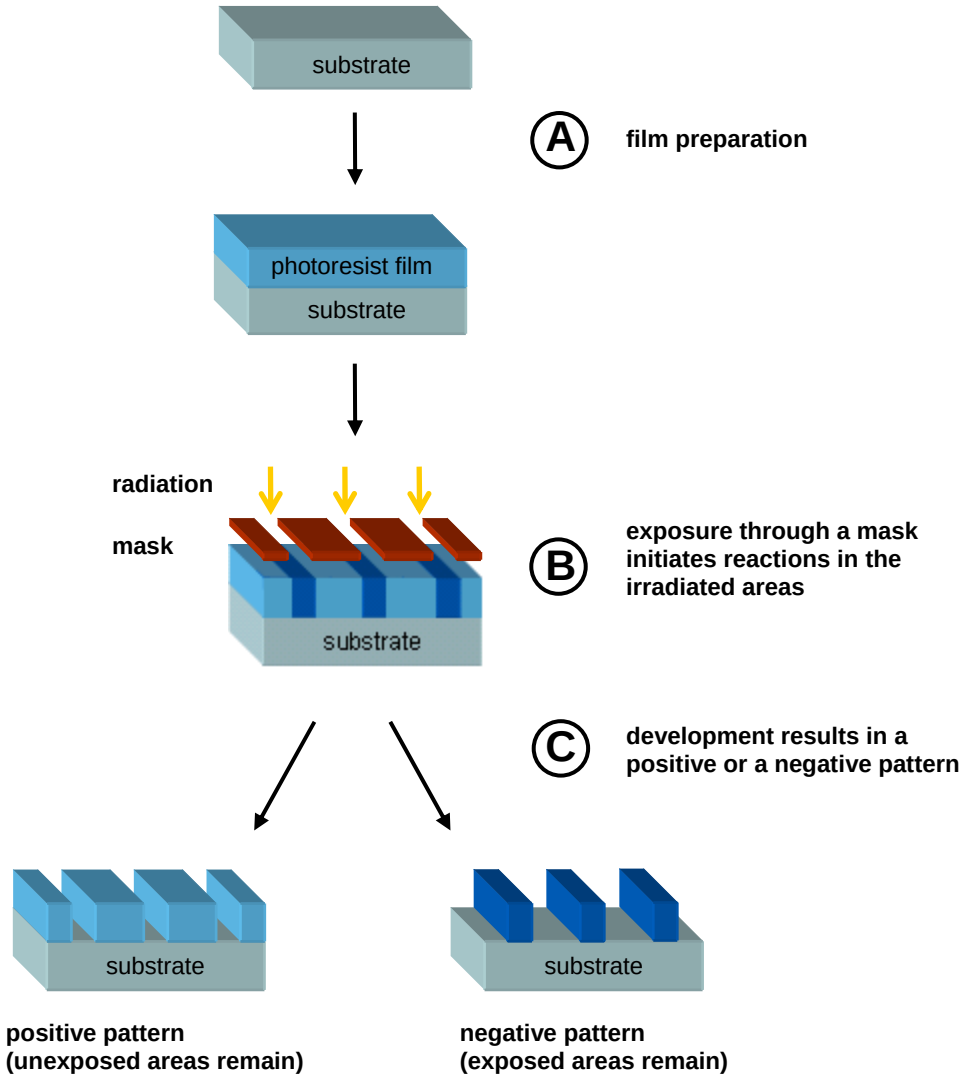


Figure 1-3. Schematic representation of the photolithography steps: film preparation (A), the exposure through a mask (B) and the development (C) to remove either the exposed parts which results in a positive pattern or the unexposed parts which results in a negative pattern.

First, the resist has to be applied onto a substrate (film preparation, Fig. 1-3, A). Second, the resist is irradiated through a mask to cause reactions in the exposed regions (Fig. 1-3, B). Third, the part of the resist which is more soluble is removed. This step is called development and results in a pattern on the substrate (Fig. 1-3, C).

Resists are divided into two categories: positive tone and negative tone resists. Such resists that give patterns by the unexposed parts are called *positive tone resists* because they look like an exact copy of the mask. This is achieved by removal of the exposed parts in the development step, e.g. typically the light induced reduction produced a more soluble

compound. A *negative tone resist* produces an inverse copy of the mask when irradiated and developed: the exposed parts remain on the substrate while the unexposed parts are removed.
The main lithography steps and the classification in negative and positive tone resists are illustrated in Figure 1-3. The major difference between these two types of resist lies in the application: isolated features are best printed in negative photoresist, whereas spaces and contacts prefer a positive resist.[14]
Usually, the resist is only an auxiliary means to selectively protect one or several layers underneath, e.g. a metal layer. After the above described development step, the underlying layer is partly covered by the resist pattern, and partly lies free. The accessible material is taken off by etching. Then, the metal layer parts which are protected by the residual resist are freed through the removal of the resist to give the final desired pattern, e.g. for electronic devices. This last step, i.e. the uncovering of the desired metallic structures, is called stripping. These steps can be repeated for various times with different masks if multidimensional structures, like ICs, demand for it.

1.2 Molecular Glasses

For photolithography in general, it is necessary for the employed resist films to be transparent. Because of their superb glass-forming properties, amorphous photosensitive polymer films are the most commonly used materials in this field. But also selected low molecular weight substances can show a stable amorphous phase, depending, amongst others, on their molecular design.[15-18] In contrast to many molecules which are crystalline in the solid state and thus light scattering and turbid, so-called molecular glasses possess a stable non-crystalline phase. Clear amorphous films can be produced, which makes them suitable for lithography and other applications. Together with glassy polymers, they form the broad group of glassy organic material.
In the amorphous phase, only a short-range order exists in contrast to crystals which are highly ordered. The characteristics of organic glasses are similar to those of inorganic glasses and include the appearance of free volume, isotropic properties and a glass transition.[19] They show a lower viscosity and a lower density than crystalline materials, and they are less hard and brittle. Once molten—only one time a melting point (T_m) may be observable—and cooled below this melting point, organic glasses do not recrystallize, but form an amorphous phase. In some cases, glasses can only be received by very fast cooling to prevent the time-intensive

rebuilding of the crystal lattice.[20] The amorphous phase of molecular glasses is thus typically received from a disequilibrium process[16,19] like coating from solution, evaporation or, as mentioned before, quenching. When heated again, organic glasses show a broader temperature range, in which the material softens, instead of a sharp melting transition.[20] The phase transition from an amorphous solid state to the melt is characterized by the so-called glass transition temperature (T_g). Above T_g, viscosity decreases immensely. When an organic glass is kept at a temperature above T_g but below T_m, recrystallization is possible because the molecules are mobile enough to build up a crystal lattice.[20] The crystal state of solids is thermodynamically favored, but kinetically inhibited.[21] In amorphous polymers, this inhibition is mostly due to the many configuration possibilities in a chain. Physical networks like entanglements and chemical networks influence the stability of the glassy state of polymeric and inorganic glasses. In molecular glasses, only low intermolecular interactions, which are molecular properties, have an influence on the stability of the amorphous phase.[22] Sterical hindrance and weak intermolecular interactions are of importance to prevent crystallization.

A various number of polymers like polyethylene or polypropylene show a melting point (T_m) in addition to T_g.[23] This reveals that they are semi-crystalline, meaning that the solid state is composed of crystalline as well as amorphous areas. The crystalline regions act as physical crosslinks between the amorphous regions. Such polymers are usually used above their T_g and below their T_m implying that they are soft and ductile. Usual applications of these polymers are for example foils for packaging.

Crystals and glasses can be clearly distinguished from each other by observing the temperature process when heated (or cooled). At a certain temperature—the melting point—the applied thermal energy in crystalline structures is completely used for breaking up the crystal lattice. The substance itself does not heat up further until the lattice is thoroughly destroyed. Thus, the melting point is very sharp, especially with low molecular weight compounds. When heating up a glass, there is no lattice to break up, therefore the thermal energy is used for further warming the substance.[24] The same holds for the cooling process of a crystal in which exothermic recrystallization with a sharp T_{rc} takes place from the liquid to the solid phase whilst a molecular glass exhibits a broad transition range from liquid to amorphous phase. This difference in thermal behavior is illustrated in Figure 1-4.

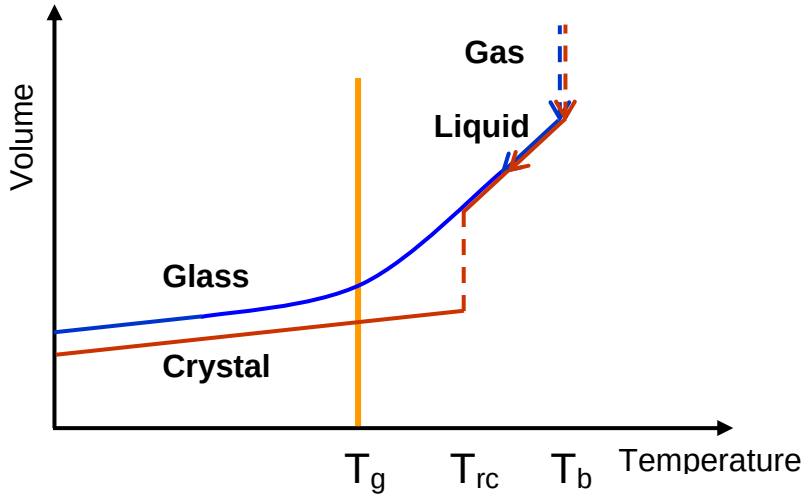


Figure 1-4. The two general different cooling paths from gas to solid phase. Crystalline materials show a sharp volume decrease at T_{rc} from liquid to solid phase. Glassy materials change only the slope upon cooling from the liquid to the solid state which is characterized by the glass transition temperature T_g (figure based on [20]).

The T_g can be determined by differential scanning calorimetry (DSC), a thermal analysis method. Typically, a small sample amount of about 10 to 20 mg in an aluminum pan is heated and cooled at defined rates. The heat flow is measured and compared with that of a reference sample, i.e. an empty pan. Changes in the heat flow are a sign of physical changes like melting (indicated by an endothermic peak), softening (indicated by a step), or crystallizing (indicated by an exothermic peak). Figure 1-5 shows a typical DSC curve of a molecular glass which was synthesized and investigated in this thesis.

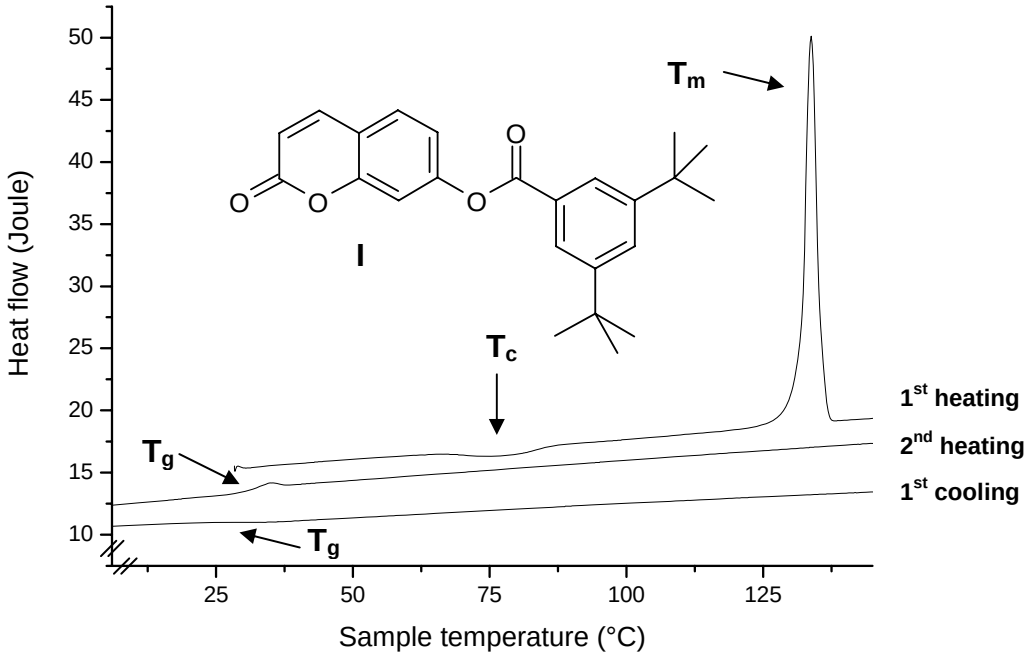


Figure 1-5. DSC traces of 3,5-Di-tert-butylbenzoiccoumarinester **I** of a weak endothermic run (heating and cooling rate: 10 K/min). The first heating curve shows crystallization (T_c) at about 75 °C and a melting point at about 130 °C. When cooled, no recrystallization is observable, but a broad, weak T_g around 25 to 35 °C is observed. The second heating, from which the T_g value is usually reported, shows a well defined glass transition temperature at 33 °C.

Generally, molecular glasses can be tailored when giving attention to some general structure rules. For example, the work of Shirota confirmed that there is coherence between the structure of organic molecules and glass-forming property.[19] He presented some guidelines for their preparation. A non-planar molecular structure and an increased number of conformers are favorable for the formation of glass-like organic material. Introducing bulky groups and expanding the molecular size decrease the tendency to crystallize and are important parameters for the stability of the amorphous state. By synthesizing molecules with a rigid core, a higher glass-transition temperature can be obtained. Other factors for an increased T_g are intermolecular hydrogen bondings, and an enlarged molecular weight.

Recently, it was found that low molecular weight, glass-like materials are of interest for lithography purposes because of their smaller molecular size compared to polymers. Envisioned are for example improvements regarding resolution in combination with a possible decrease in line edge roughness (LER) and the usage of new film preparation methods like physical vapor deposition (PVD)[15] as it is performed in this thesis. The application of low molecular weight resist (LMR) was successfully performed by Ohno et al. employing DNQ sulfonate using DUV and contact printing.[25] Shirota introduced a molecular glass for electron beam writing[26] as well as Ober et al. who prepared amorphous materials with high T_g based on star-shape molecules, calix[n]arene derivatives, dendrimers, *t*-BOC protected calix[4]resorcinarene, hexa(hydroxyphenyl)benzene and its derivatives.[27,28] Ober et al. additionally work on the usage of molecular glasses in chemically amplified resists (CARs) as shown later in Chapter 1.3.
A high glass-transition temperature is of advantage for lithographic applications because it increases the temperature range in which the resist in various process steps can be treated: Using process temperatures which are significantly above T_g cause the film and thus the created structures to soften and dewet which downgrades the quality of the produces features.

1.3 Chemically Amplified Resists and Photo Acid Generators

As much as photoresist systems differ from each other, they have in common that a reaction is caused or at least induced by light irradiation. Sometimes the molecules are self-reacting, but in many cases one or several auxiliaries are necessary. Common photoinitiators cleave when

exposed to specific wavelengths to give radicals, cations or anions. These reactive molecules initiate or catalyze reactions between suitable reagents.

An important class of photo-reactive molecules is that of photoacid generators (PAGs). Upon irradiation with light, these substances generate very reactive intermediates, and subsequently protons. They have been found useful for the preparation of coatings, adhesives, inks, and lithographic purposes[29] to initiate acid sensitive reactions, e.g. polymerizations, to catalyze crosslinking or condensation reactions, deprotection, or depolymerization.[30] Thus, in respect to photolithography, they can be used for negative as well as for positive photoresists. In general, the solubility of the exposed resist parts is changed by these reactions.

PAGs are often parts of chemically amplified resists (CARs). The name implies that one proton catalyzes many subsequent reactions. The turnover rate (catalytic chain length) is usually between 800 and 1200 cycles.[31,32] Thus, the light sensitivity is enhanced, the reactions take place faster. The original meaning of the term CARs was limited to such reactions in which the generated acid deprotected other resist components und thus increased their solubility in polar solvents. In contrast to classical microlithography, the quantum yield, also called quantum efficiency (the number of acid moieties generated per photon absorbed[32]), of PAGs is quite high, a reasonable value is about 0.5.[33] This means that by a catalyzed cascade of reactions the irradiated portion is almost or completely converted.[34-36] Because of this effectiveness, improved sensitivity, and contrast they are especially interesting for decreased feature sizes in sub-0.5-µm lithography (see Ch. 1.1.1).[30]

Typically, a short heating of the irradiated film after irradiation, the so-called post-exposure bake (PEB) or postbake, is necessary to activate the acid catalyzed reaction[2] and to increase the mobility of the acid.[37] Depending on the used PAG and CAR, the time and temperature of the PEB can have a significant influence on the sensitivity,[2] contrast and resolution of the resist.[32] A maximization of the yield and thus the highest possible solubility difference between exposed and unexposed areas is important for an improvement in image contrast.[30,32]

An example of the general acid catalyzed reaction between a phenol and an acid labile component used in this work is given in Figure 1-6. When at least one of the reactants is polyfunctional, a chain extension or crosslinking reaction occurs. This reaction results in a *negative pattern* because the formed product is not soluble in basic aqueous tetramethylammonium hydroxide (TMAH) developer solution in contrast to the phenol.

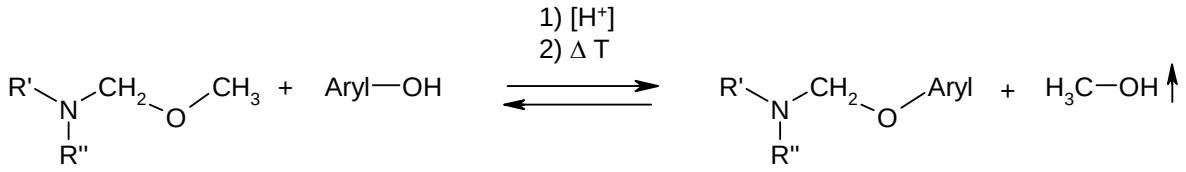


Figure 1-6. Structural representation of an acid catalyzed reaction between a phenol and an acid labile component used for the preparation of negative tone photoresists.[38]

A typical way to obtain *positive patterns* of CARs is a PAG catalyzed deprotection reaction in which a polarity change from a non-polar to a more polar system and thus a solubility change is induced (Fig. 1-7).[29,39] The development takes place in a basic aqueous solution like TMAH to give a positive tone pattern. Using an organic solvent as developer would result in a negative tone pattern.[40,41]

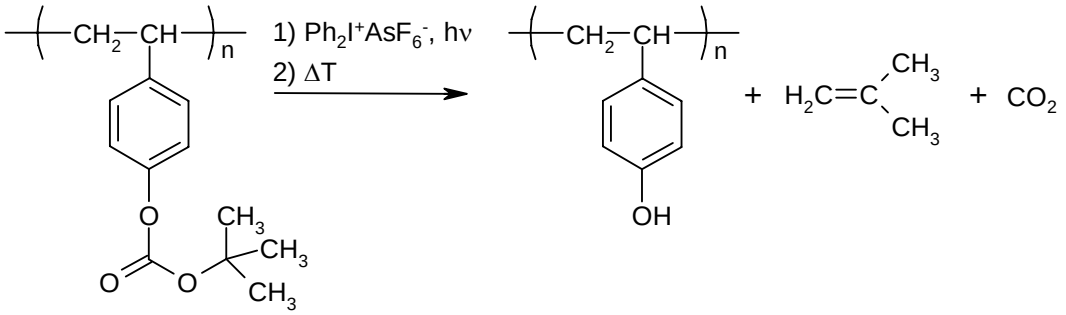


Figure 1-7. Structural representation of a polymer-analogous acid catalyzed deprotection reaction. A polarity change of the polymer is achieved by cleavage of the *t*-Boc protection group due to acid formation of a PAG by irradiation (figure based on [29]).

The material class of photoacid generators is divided into *ionic* and *non-ionic* species.[29] Examples of both types are shown in Figure 1-8.

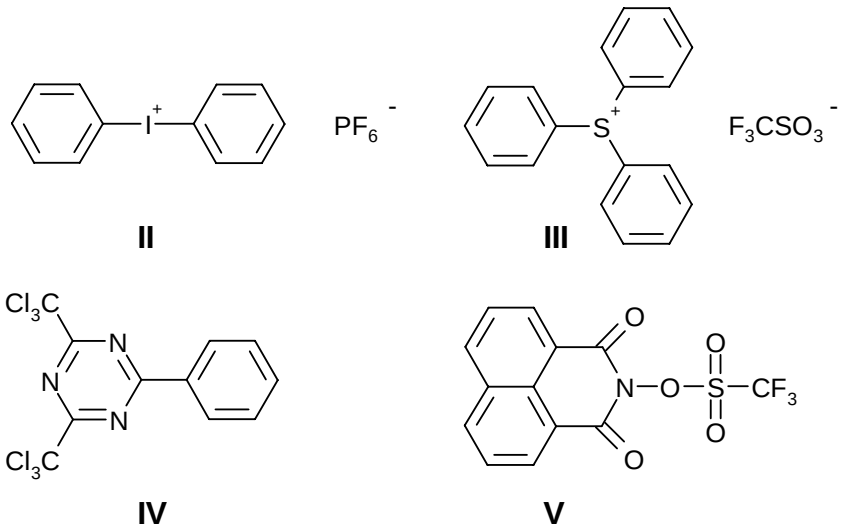


Figure 1-8. Examples for ionic (**II** and **III**) and non-ionic (**IV** and **V**) photoacid generators: diphenyliodonium hexafluorophosphate **II**, triphenylsulfonium triflate **III**, 1-phenyl-3,5-bis(trichloromethyl)triazine **IV**, and *N*-hydroxynaphthalimide triflate **V**.

Ionic PAGs often consists of diaryliodonium or triarylsulfonium salts. These are typical examples for a group called onium salts, which was first used as photoinitators for cationic polymerization.[42-44] While, because of their ionic character and the radical intermediates, they might be problematic for nonpolar polymer matrices, they offer various advantages as PAGs. By modifying them to be thermally stable and be adjusted to special wavelengths they are fitted to work very well with various systems. The poor solubility in many organic solvents remains a disadvantage of ionic PAGs, though.[29] An example for the proton formation of an ionic PAG **II** induced by irradiation is given in Figure 1-9.

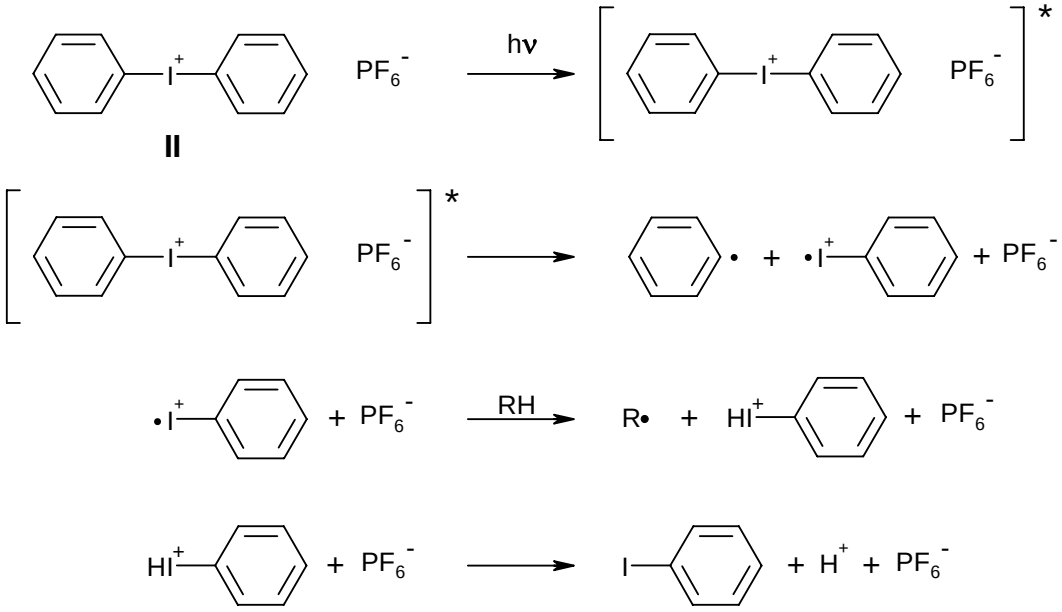


Figure 1-9. Structural representation of proton generation of the ionic PAG diphenyliodonium hexafluorophosphate **II** when exposed to wavelengths smaller than 400 nm.[42]

A well-known example for *non-ionic PAGs* is the class of nitrobenzyl esters.[45,46] Since, in contrary to ionic PAGs, no free radicals are produced in the main photochemical event[47] and the nitro group is an inhibitor for radical processes, they are well suitable for minimizing secondary reactions.[32] By introducing suitable bulky groups at certain positions, their thermal stability can be increased significantly.[47] Their solubility in common organic solvents and polymers is an advantage compared to ionic PAGs,[29] whilst their smaller catalytic chain length prevents the usage in common industrial applications if ionic PAGs are suitable as well for the considered applications. An example for the irradiation induced acid formation of the non-ionic PAG group of 2-nitrobenzyl esters is shown in Figure 1-10.

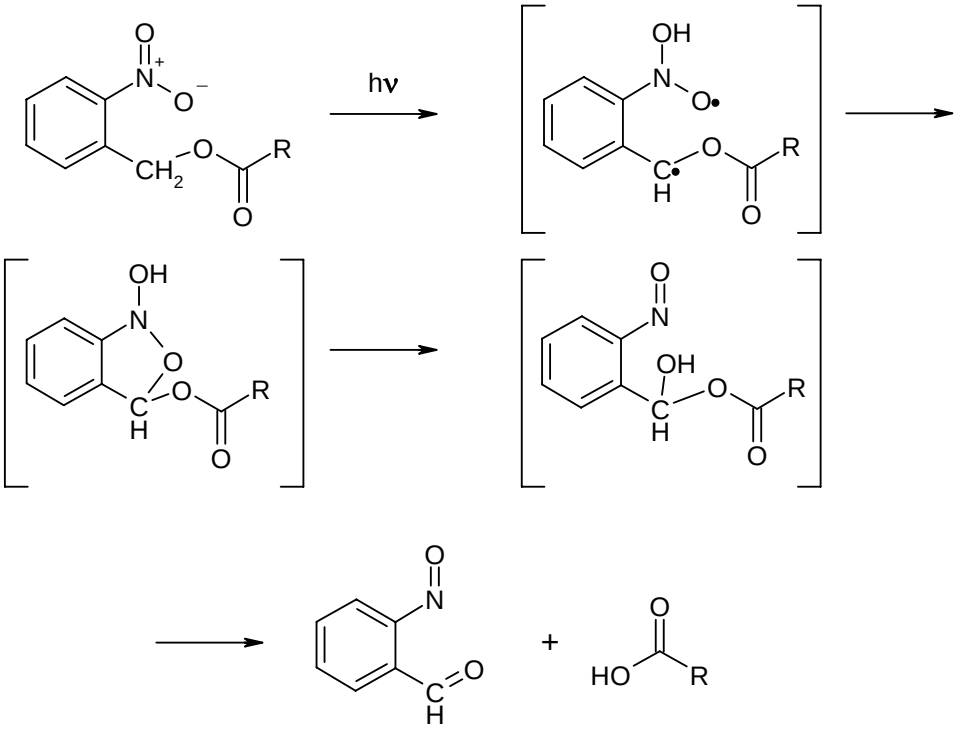


Figure 1-10. Structural representation of the acid generation by intramolecular photorearrangement of 2-nitrobenzyl esters (figure based on [29]).

Ionic and non-ionic PAGs differ not only in thermal stability and solubility in various solvents. Usually, resists containing a non-ionic PAG often show a lower sensitivity than the same resist with an ionic PAG, implying that a higher exposure dose and thus a longer exposure time are required. This is an important cost factor in industry. A fourth important parameter of PAGs is the above mentioned catalytical chain length (moles of photoreaction per mole of generated acid).[47]

Non-ionic PAGs often contain sulfonic acid moieties which generate strong, low nucleophil organic acids when irradiated.[30] Some functional groups, such as triflate (trifluoromethanesulfonate), are used in both ionic and non-ionic PAGs. Triflate is a favorite PAG component since it is a stable moiety,[36] and the resulting triflic acid is very strong, it is a so-called super acid. The type of the resulting acid can influence the quality of the produced features. For example, small volatile molecules like hydrochloric acid show a high diffusion and might catalyze reactions in adjoining unexposed areas. In consequence, line sharpness and resolution suffer from excessive acid diffusion which is also influenced by temperature, the polarity of the resist material, side reactions which prematurely destroy the acid ,[32] and potential solvent residues in the photoresist.[39] In summary, thermal stability, quantum yield, catalytic chain length, and solubility are the most important specifications for commonly used PAGs.[47]

Chemically amplified resist (CAR) compounds do not necessarily need to contain polymers, but can also be composed merely of low molecular weight compounds. Ober et al. reported negative and positive CARs based on molecular glasses containing multifunctional groups, a PAG and a crosslinker.[48,49] Resist films consisting of such low molecular weight compounds can be spin-coated like polymer resist films, but can also be prepared solvent-freely by physical vapor deposition (PVD), which is a core element of this thesis.

1.4 Vacuum Deposition Techniques

1.4.1 Overview and general principles

As illustrated in Figure 1-3, the first step in photolithography is the application of the resist as a thin film onto the substrate. There are various possibilities to produce films of different layer thicknesses. Casting from solution is the main method in industry because it is fast and reproducible. Suitable solvents need to show good film building qualities and a suitable vapor pressure, i.e. it must not evaporate instantly after casting, but should evaporate completely after gentle heating. Common casting solvents include THF and PGMEA. Usually, the material is dissolved with a ratio of 10 to 20wt.%, and then applied onto the substrate (e.g. silicon wafer, or glass slide). A typical method is spin-coating in which the substrate is fixed by vacuum suction on a rotating plate. The resist solution is dripped onto the substrate, and then the rotation starts. The film thickness depends on the dilution of the solution and the revolutions per minute (rpm). The typical rotation number is in the range of 1,000 to 4,000 rpm. Solution casting methods include also doctor blading, in which a device with a defined gap is moved over the substrate to cast the solution uniformally. Other film-forming methods are spraying and dipping. Solution casting is finished by a so-called post application bake (PAB), also called pre-bake. In this step, the substrate with the film is put onto a hot stage or in an oven to remove the solvent completely.

A completely different approach is the direct deposition of organic compounds from the gas phase. Generally spoken, by evaporation, the material is in gaseous state, or by transportation through a carrier gas, the material is nebulized. If the material should deposit exclusively on the cool substrate, the chamber parts which are supposed to remain clean must be heated. Normally, the evaporation is achieved by direct heating, but also other methods like standard

radio frequency magnetron sputtering equipment—in which the material powder is bombarded by low energy He ions and electrons at relatively low pressures (10^{-10} Pa)[50]—or electron beam evaporation are reported.[51]

The advantages of evaporation techniques are the production of very controlled, smooth films, the arbitrary film thickness, the preparation of subsequent film layers or thickness gradients, the possibility to use every kind of substrate, the employment of combinatorial techniques (see Ch. 1.4.2) and in addition the application of substances which are not soluble enough for solvent casting methods. The disadvantages are the high initial price of the vacuum chamber and the limitation of substances regarding their thermal stability and volatility.

Many different substances can be used for vapor deposition. Quite common is the deposition of metals like gold or aluminum as electrode materials for devices such as solar cells, organic light emission devices (OLEDs), or organic field-effect transistors (OFETs). Organic material can be used for this film preparation technique as long as the thermal stability is sufficient. The vapor pressure of the substances and the interactions between the material and the surface of the substrate are also of importance, since the substances might desorb from the substrate because of the high vacuum (in the range of 10^{-6} mbar). A possibility to improve the adsorption is to cool the substrate. Using suitable materials, electro-optical devices can even be completely prepared by vapor deposition.[52-54] Finally, also ceramic solids like Al_2O_3, SiO_2, or $MoSi_2$ can be prepared on substrates by evaporation of precursors, or in combination with metal deposition.[55]

The usual prepared film thicknesses are in the nanometer up to a couple of micrometers range. The produced layers have very different applications—from coatings protecting against abrasion[56] or oxidation, the production of orientation layers,[57] to photoresist films.[58]

There are two different methods of vacuum evaporation: *physical vapor deposition* (PVD), and *chemical vapor deposition* (CVD). Vapor deposition polymerization (VDP) is a special case of CVD. The two mentioned methods differ in the way the thin film is prepared on the substrate. Using *CVD*, the condensed material did not exist before—a chemical reaction of the evaporated substances occurs either in the gaseous phase or when depositing, often by a catalytical impact of the substrate.[59] Usual reactions in CVD include chemical reduction, or thermal decomposition.[55] The latter case is illustrated in Figure 1-11 in which the precursor C is brought into gas phase and then being transported into the reaction vessel. After decomposition, the cleavage product B is removed while the desired material A deposits on the susbstrate to form a film. The applied vacuum is generally weaker than that used for PVD

(even atmospheric CVD chambers are in use), and the main transport mechanisms are diffusion and convection processes.[60]

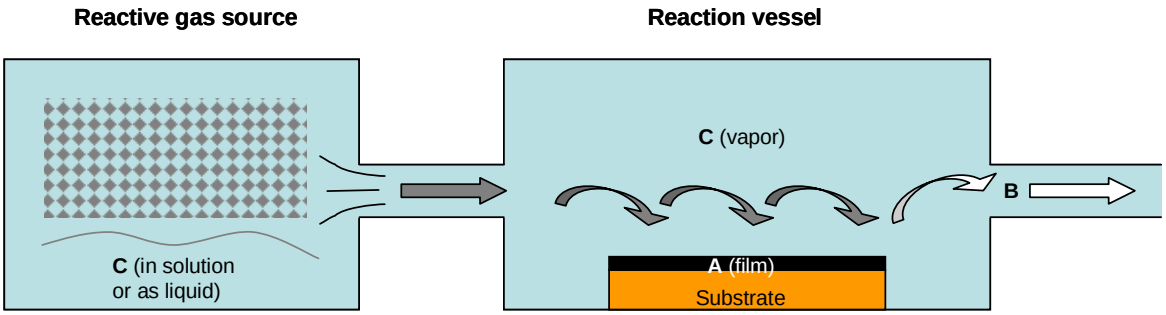


Figure 1-11. Schematic representation of a CVD reactor in which substance C reacts to form the desired material A on the substrate by thermal decomposition when depositing (figure based on [60]).

Regarding *physical vapor deposition* (PVD), the evaporated material A remains unchanged. Under high vacuum (in the range of 10^{-6} mbar) and heating, it is transferred from the source to all cooler surfaces, including the substrate, to form a thin film. A simplified scheme of a PVD chamber is shown in Figure 1-12. PVD can only be operated under high vacuum, and the necessary temperatures are usually lower than that of CVD. Depending on the material, temperatures up to 2000 °C are employed.[59]

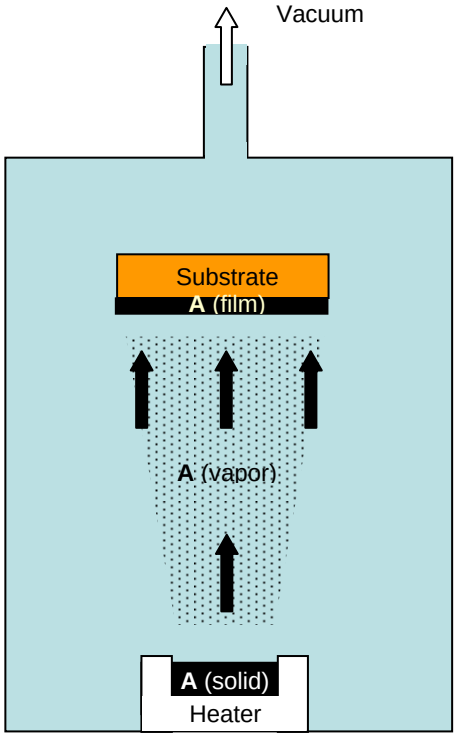


Figure 1-12. Schematic representation of a generic PVD reactor. Substance A is heated in high vacuum until evaporation occurs, and then the vapor deposits on the cooler substrate to result in a uniform film.

The latest development in PVD technique is vertical in-line evaporation processing. Several glove boxes and vacuum chambers containing various sources and sputtering facilities are connected to each other. The substrate is transported through this fabrication line and stays under continuous vacuum from the first to the last step. This efficient method could already be successfully established for an in-line OLED fabrication system at Fraunhofer Institut für Photonische Mikrosysteme in Dresden.[61]

With vapor deposition polymerization (VDP), thin polymer films such as polyimides can be prepared on a substrate.[57] The monomers are evaporated and deposited as a thin layer on the substrate. The film is then polymerized by irradiation or heat, either directly in the chamber without breaking the vacuum[62] or outside the chamber. Not every polymer can be produced by VDP, though. Again, the material has to be thermally stable. Additionally, in some rare cases the ceiling temperature of the generated polymer is an important parameter that has to be considered to prevent depolymerization above a certain temperature.

1.4.2 Combinatorial physical vapor deposition

As stated above, the material which is evaporated and deposited by PVD remains unchanged—no chemical reactions occur in the chamber, as opposed to CVD. The PVD evaporation chamber which is employed in our group is equipped with a special setup consisting of shutters and masks: the usage of those combinatorial techniques enables the quick manufacture of gradients and sectors *on the same substrate* in *one combinatorial experiment* without breaking the vacuum or opening the chamber.

For example, a movable shutter mask between the source and the substrate allows the preparation of a *linear gradient* of one evaporated substance on the substrate if the movement is continuous, or of a *step gradient* if the movement is stepwise (see Fig. 1-13).[63] By doing so, the influence of e.g. different layer thicknesses in organic light emission devices (OLEDs) can be investigated.[52,64]

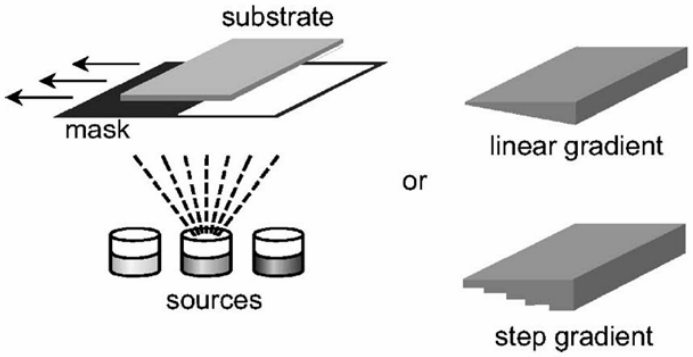


Figure 1-13. Schematic representation of gradient preparation. A continuous movement of the shutter mask leads to a linear thickness variation; a stepwise movement of the shutter mask results in a step gradient.[63]

The preparation of different sectors, a so-called *sector library*, on one substrate is realized by the usage of various masks and the possibility to rotate the substrate. This technique was applied to investigate an influence of the layer sequence of several substances (see Fig. 1-14) on the performance of OLEDs.[63,64] First, one substance is allowed to deposit on the complete substrate. After a defined layer thickness is reached, the evaporation process is stopped. A mask is put into a defined position to partly cover the substrate.

When evaporating the second substance, it can only deposit on one half of the substrate. By either using a third mask or rotating the substrate 90° after the second evaporation, the third substance also deposits only on defined areas of the substrate. At the total, four different sectors of three different substances are created.[63]

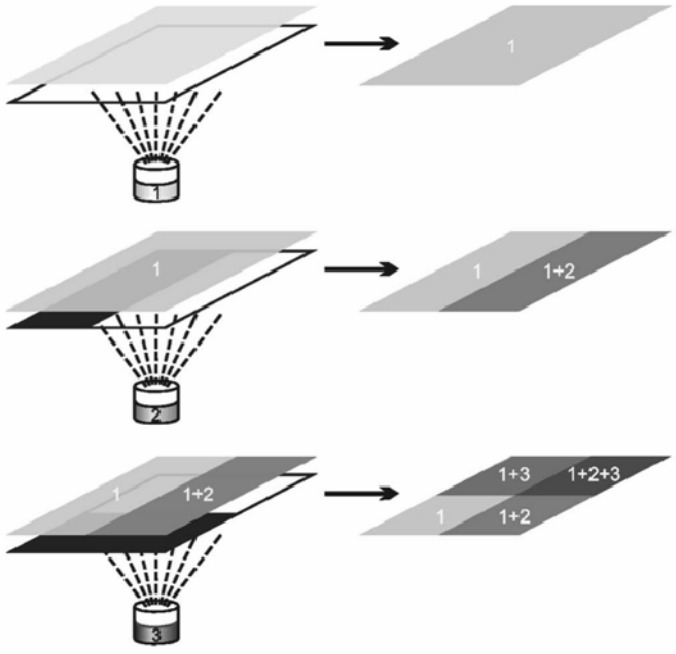


Figure 1-14. Schematic representation of the sequential preparation of a four sector library with different layer sequences by using either three different masks or two masks and rotating the substrate 90° before the last step.[63]

In the above stated example, several substances were evaporated subsequently. It is also possible to *evaporate several materials simultaneously* (coevaporation) as shown in Figure 1-15[64] and Figure 1-16.[58] By changing the temperature in the sources and thus the evaporation rates of the substances, the created sectors differ in the relation of the used materials. Such a sector library is useful for optimizing the composition of the substances and was performed with vapor-depositable photoresist materials in this thesis.

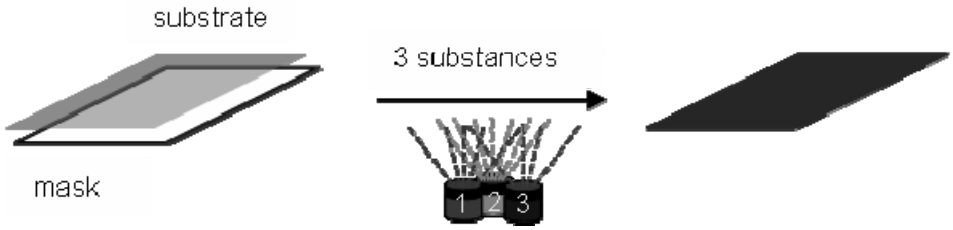


Figure 1-15. Schematic representation of the simultaneous evaporation of three substances.[64]

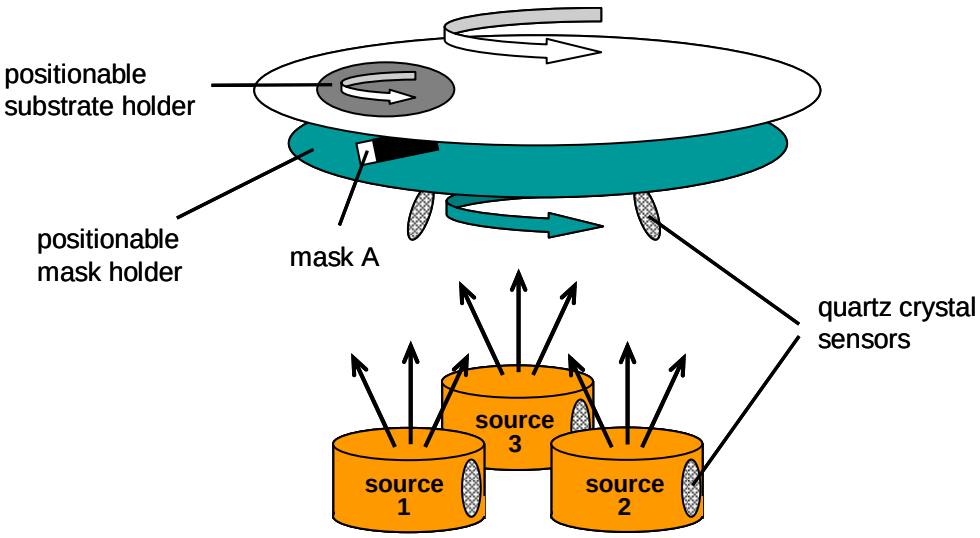


Figure 1-16. A more detailed schematic representation of the coevaporation process in the PVD chamber, applying combinatorial techniques (see below) to produce sectors with different compositions.[58]

After subsequent experiments like exposure and development, the differing sectors, which were produced under the exact same evaporation conditions, are compared with each other so that the influence of the investigated parameters can be easily monitored and judged.

For the actual PVD experiments, about 150 mg of the thermally stable material is put into a quartz glass tube which fits into the effusion source. Using these sources (see Fig. 1-17), the generated heat can be adjusted more precisely than using normal resistance heating, which is an advantage especially for the controlled evaporation of organic material.

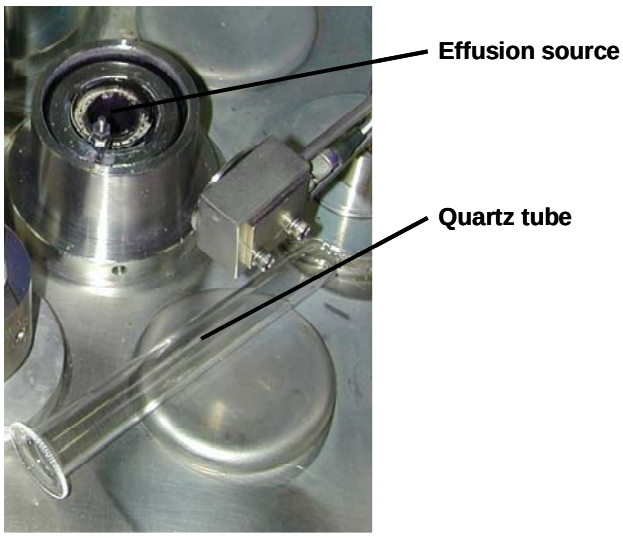


Figure 1-17. Picture of an effusion source and the relating quartz tube in which the solid material is filled to be evaporated.

Movable metal hatches, so-called shutters, below the substrate and above the source allow a controlled deposition. By providing not only one, but various sources, either coevaporation or the preparation of different subsequent film layers is possible without opening the vacuum chamber. If each of the three sources is equipped with a sensor (quartz crystal microbalances), specific evaporation rates and film thicknesses can be measured (see Fig. 1-18). Two more sensors are installed about 25 cm above the sources to track the evaporation process near the substrate.

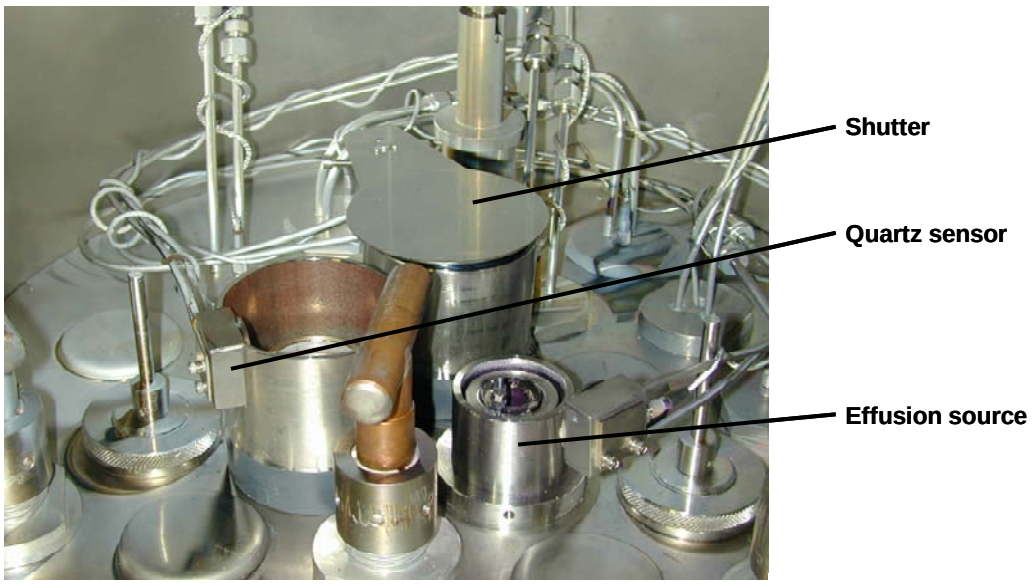


Figure 1-18. Detailed picture of the sources area in the PVD chamber which is used for coevaporating up to three substances.

As mentioned earlier in this chapter, the usage of a suitable mask below the substrate lets the vapor deposit only on desired areas. By putting several masks into a positionable mask holder below the substrate, the possibilities for the preparation of samples increase significantly. In combination with coevaporation, different sectors with different compositions on the same substrate can be prepared in one vapor-deposition step without breaking the vacuum to change material or masks. The complete substrate set-up with positionable substrate holder, positionable mask holder and an example selection of masks which allows combinatorial preparation of different film thicknesses, compositions and films is shown in Figure 1-19.

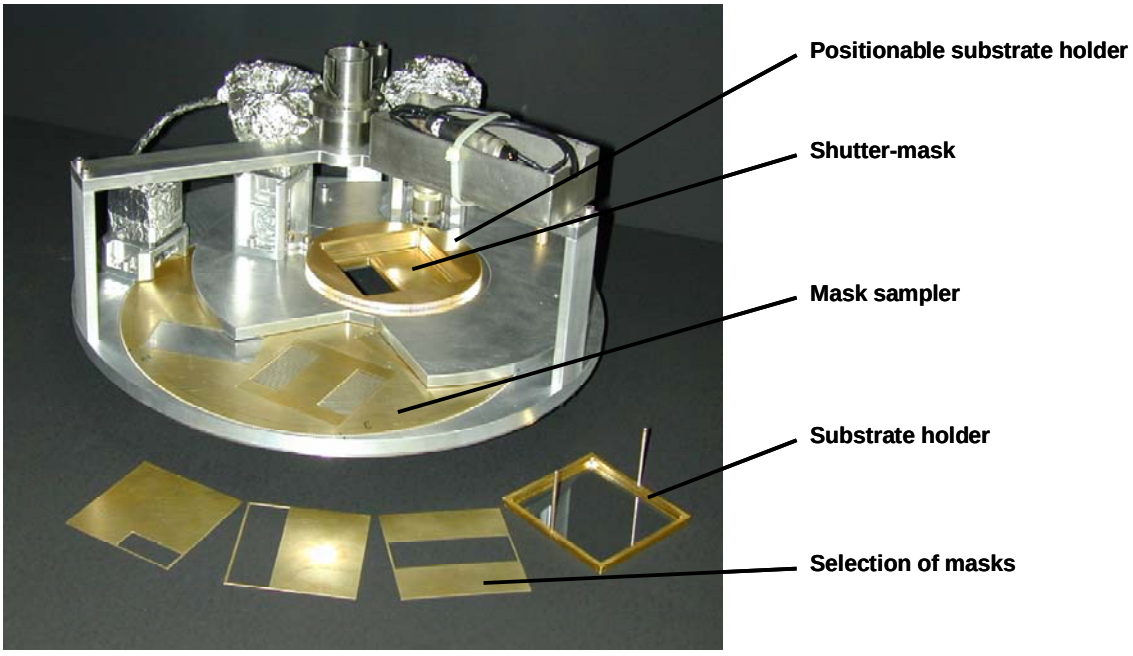
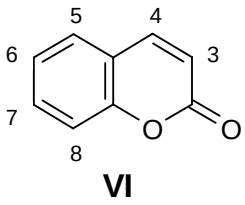


Figure 1-19. A rotating set-up provides several masks and a positionable substrate holder with a shutter to produce a sector library on the same substrate in one vapor-deposition process.

1.5 Photoreaction of Coumarins

Coumarin (2*H*-1-benzopyran-2-one) **VI** is a natural substance that can be found in some plants like woodruff (see Fig. 1-20) in which it determines the typical odor[65] after withering.[66]

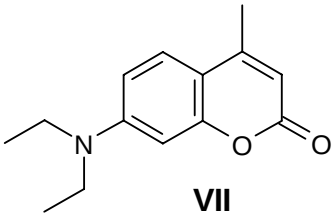


VI

Figure 1-20. Coumarin **VI** can be found naturally in withering woodruff. These woodruff plants grow near to Bayreuth in Sanspareil (picture used with permission of Katy Bosworth).

It is a colorless solid (T_m 70.6 °C) with a hay-like odor. Coumarin is widely used in fragrances, and in galvanization as a brightener.[65] Since 2005, because of its allergenic potential coumarin must be labeled in the European Union as perfume ingredient in cosmetics if the concentration exceeds a certain value.[67] In animal experiments, liver-toxic and carcinogenic properties were observed. It is not yet clear if these results can be assigned to humans.[66] By the International Agency for Research on Cancer (IARC), coumarin is not classifiable as to its carcinogenicity to humans.[68] Treating coumarin with dilute alkali solution, it hydrolyzes to the corresponding salt of *cis*-2-hydroxycinnamic acid.[69] This is the kinetically preferred isomer. After a certain time or by heating with concentrated alkali, the thermodynamically preferred isomer, the salt of *trans*-2-hydroxycinnamic acid, is formed. Since coumarin is the main body for various biological active substances, it became interesting for medical purposes. Coumarin itself does not show anticoagulant properties, but possesses anti-inflammatory activity, antipyretic effects, and therapeutic effects in high

protein lymphoma chronic infections, disorders of the immune system and cancer.[70] Psoralen, a linear furanocoumarin with photosensitizing properties, serves in combination with long-wave UV light as treatment against psoriasis, a skin disease. Because of the anticoagulant properties of some coumarin derivatives (especially those of 4-hydroxycoumarin[66] and dicoumarol[70]), there is a wide range of applications possible. They are used for such different appliances as rodenticides (e.g. Cumatetralyl) and as medicaments against thrombosis (e.g. Warfarin® and Marcumar®).[71] Other coumarin derivatives show a strong fluorescence, like 7-dimethylamino-4-methylcoumarin **VII**, and are employed as laser dyes.[72]



VII

In solution, coumarin, as well as many of its derivatives, undergoes a [2+2] cycloaddition (see Figure 1-21) to form a dimer when irradiated. This reaction is well known and examined.[73]

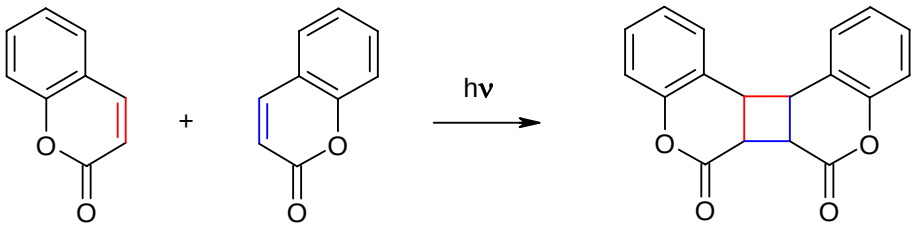


Figure 1-21. Photodimerization by light irradiation of two coumarin **VI** molecules in solution to give dicoumarin.

Under normal circumstances, this reaction cannot be triggered by thermal energy, but recently it was shown that coumarin and thiocoumarin can be dimerized by heating in high vacuum when they are existent in inclusion crystalline complexes.[74]

There are four possibilities how two coumarin derivative molecules can bind via cycloaddition. The photodimerization can theoretically result in following isomers, syn head-to-head **VIIIa**, anti head-to-head **VIIIb**, syn head-to-tail **VIIIc**, and anti head-to-tail **VIIId** as shown in Figure 1-22 for two coumarin molecules.[75]

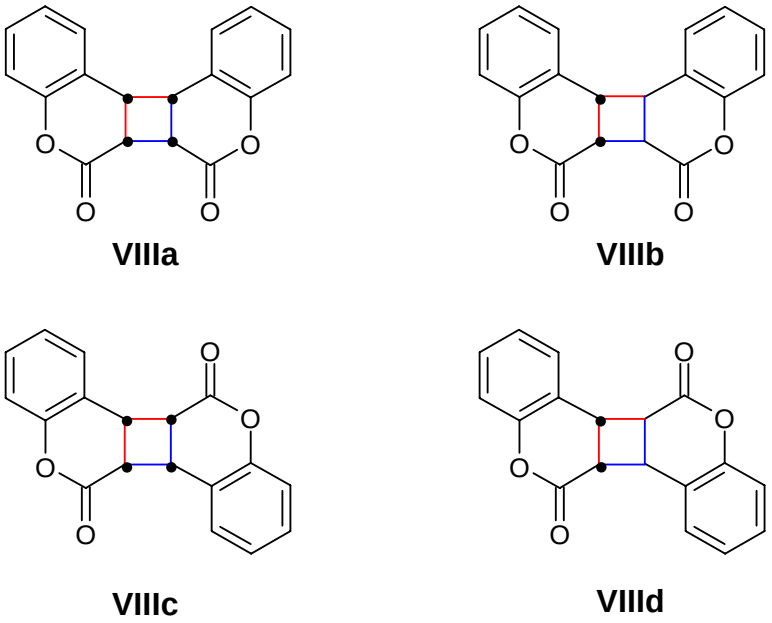


Figure 1-22. When irradiated in solution, four possible isomers can be theoretically formed from coumarin **VI**.[75]

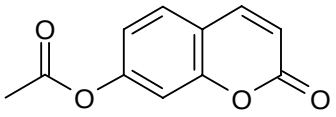
The generating probability is not the same for each isomer, though. Many publications addressed this issue, mostly investigating the photodimerization in different solvents. It was found that, depending on parameters like solvent or sensitizer, some isomers are favored. For example, **VIIIa** is formed from **VI** in methanol or benzene from the first excited singlet state in an inefficient photoreaction ($\varphi < 10^{-5}$ at a concentration of 0.02 M coumarin).[76] But when triplet-sensitized, **VIIIb** is the main product with a much higher quantum yield ($\varphi \sim 0.1$),[77] independent of the solvent.[73,75] The dimerization rate can be increased by a higher polarity of the solvent[78] or, very efficiently, by adding Lewis acids.[79] In the first case, **VIIIc** was additionally found.

Substituted coumarin derivatives are found to form preferably syn dimers from the singlet and anti dimers from the triplet state.[80,81] Not every coumarin derivative dimerizes when irradiated, though.[82] There are also examples like those with an amino donor at position C7 which dealkylate and show a photoreduction of the C3/C4 double bond when exposed to light.[83]

The dimerization of coumarin is reversible. When **VI** is exposed to wavelengths shorter than 300 nm, the cyclobutane ring preferably cleaves and the monomers are reformed.[78] Because of this unwanted reaction, it is important to use only irradiation sources which emit light longer than this critical wavelength, as was performed in this thesis.

The photoreaction of coumarin derivatives *in the solid, crystalline state* is a special field of research. Some reactions do not occur in the solid, but only in dissolved state. For example, for the intensively investigated coumarin **VI** photodimerization takes place in solution, but it does not undergo dimerization in its solid, crystalline state.[77,84] When it is resolidificated from a melted mixture with crystal lattice-controlling substances such as antipyrine or phenanthrene (molar ratio 1/3 to coumarin) and exposed to UV light, products can be identified, though.[85] The resulting dimers are in most cases the syn head-to-head dimers. It is assumed that due to the cocrystallization, the packing mode of coumarin in the crystalline state is changed. Other additives like naphthalene had no effect.

When coumarin is substituted, some derivatives are known to photodimerize in solid, crystalline state. For example, an acetoxy group in position C7 (7-acetoxycoumarin **IX**) lets the topochemical photodimerization occur without any issues, stating that the functional group plays an important role as steering agent.[86,87]



IX

Interestingly, the dimerization of other coumarin derivatives like 7-methyl coumarin or 4-methyl-6-chloro coumarin in the solid state show a significant induction period in the irradiation time vs. percentage of yield plot[88] while 7-acetoxy coumarin does not show such an initial induction period.[89] This indicates that the former dimerizations are defect initiated while the latter one is topochemically controlled. Such differences in the dimerization reaction were also found comparing the photoreaction of solid 7-fluoro-4-methylcoumarin and 6-fluoro-4-methylcoumarin. The 7-substituted derivative dimerized topochemically controlled and gives anti head-to-tail dimers. The photodimerization of the 6-substituated derivative gives syn head-to-head products. It is defect initiated and in dependency of temperature.[90] The initiation by defects in the lattice might be a reason for some solid state photoreactions which violate the topochemical principles such as nonparallel double bounds[89,91,92] or a bigger distance between the bonds.[93,94] In such cases, molecular motion plays an important role in photoreactivity,[95-97] as well as orientational flexibility in the molecules and their environment might be of importance.[96]

One of the aims of this thesis was to synthesize, characterize and investigate novel coumarin derivatives which form a glassy solid state.

2. AIM OF THE THESIS

The requirement for smaller structures, e.g. applied in integrated circuits, is still one of the most important driving forces in the research field of lithography. The patterns are generated by the exposure of photosensitive material, so-called photoresists, through a mask and the subsequent development in which either the exposed areas or the unexposed areas are removed. In industry, polymers are common components of photoresists. In the last ten years, approaches towards low molecular weight, glass-like substances ("molecular glasses") have been made by Shirota[19,98] for the usage in electronic and optoelectronic devices and by Matsui et al.,[99] Ueda et al.,[100] and Ober et al. in the field of lithography.[28,49,101] The reduction of the molecular size itself is promising to conduce to a further diminution of the size of producible structures.

The aim of this thesis is to *employ low molecular weight photoresists for a solvent-free film preparation* method via physical vapor deposition (PVD) as well as to establish an *all-dry photolithography process* with newly synthesized molecular glass materials. Film fabrication by PVD has the advantage to improve film qualities like dust- and pinhole-free, smooth surfaces and implies a reduction of waste. By applying combinatorial techniques, PVD allows several deposition options like subsequent layers, gradients or composition variations on the same substrate as an efficient method for the optimization of parameters like film thicknesses, compositions and so on. Low molecular weight photoresist systems with two different types of mechanisms as well as the corresponding photolithography processes are supposed to be investigated in this context.

Physical vapor deposition of molecular glass photoresists as a new route to chemically amplified patterning: The first resist type is that of *chemically amplified resists* (CARs) in which first an acid is generated by irradiation which then catalyzes subsequent reactions. Within this thesis, several described ternary CAR systems should be investigated for their suitability for PVD. Thus, the main goal is to identify and employ qualified compounds to develope vapor-depositable CAR systems. Thermal stability and glass-forming properties are important features in regard to this deposition method and preparation of photoresist films.

These properties have to be investigated in prescreening experiments like sublimation and vapor deposition, and by analytical methods like TGA, DSC and HPLC. The composition of each of the CAR systems and exposure doses should be optimized by applying combinatorial methods. By preparing various sectors with different compositions on the same substrate via PVD and applying different exposure doses to each of these sectors, the optimized parameters can be efficiently determined. A characterization method to determine the compositions on the substrates has to be established. Additionally, the dilution of the development solution, by which the unexposed areas of the photoresist are removed, and the development time should be optimized for each of the investigated CARs. In chapter 3.1 and 3.2, the results of the above stated investigations on the subject of the suitability of several low molecular weight, glass-like CARs for vapor deposition are summarized, while a detailed description can be found in publication A1 and publication manuscript A2 in the appendix.

Synthesis and all-dry lithography based upon low molecular weight coumarin derivatives: The second molecular glassphotoresist type which should be developed is supposed to realize an all-dry photolithography process. It is based upon low molecular weight coumarin derivatives which are literature-known for undergoing a [2+2] cycloaddition in dissolved and solid crystalline state when exposed to wavelengths above 300 nm. For this thesis, several low molecular weight coumarin derivatives should be synthesized towards glass- and film-forming properties, thermal stability and vapor-depositability. The products have to be characterized by various analytical methods. The material should be evaporable and form amorphous films when deposited by PVD. The influence of exposure doses should be investigated. A dry development process has to be established, utilizing the difference in physical properties between the monomers and the products which are generated in the exposed areas. By thermal treatment under high vacuum, the monomers should evaporate while the prior exposed material remains on the substrate to form the patterns. A summary of the results of the experiments regarding the suitability of several low molecular weight, glass-like coumarin derivatives as vapor-depositable and dry-developable photoresists can be found in chapter 3.3 and 3.4. Detailed descriptions of the performed investigations in publication manuscript A3 and publication manuscript A4 are given in the appendix.

3. CHEMICALLY AMPLIFIED RESISTS

The main resist materials for lithography are based on polymers. They show an extension of several nanometers which might become a significant limiting factor to the resolution of the produced features regarding the proceeding diminution in lithography. Low molecular weight organic substances that form stable amorphous phases, so-called molecular glasses, are becoming more and more interesting to this research field. Because of their smaller sizes, they are investigated as a substitute to the commonly used large macromolecules.

Chemically amplified resists (CARs) consists of at least two components of which one is a photoacid generator (PAG). When exposed to suitable radiation, an acid molecule is generated from a PAG molecule after several intermediate steps. By a subsequent post-exposure bake (PEB) step, a proton initiates further reactions, e.g. deprotection or crosslinking reactions, which are related to a solubility change of the exposed parts of the resist. The proton generated of one PAG molecule can catalyze hundreds of acid sensitive reactions (expressed by the specific catalytic chain length of the PAG), and the quantum yield (see Ch. 1.3) is remarkably high. Thus, the sensitivity and efficiency is immensely increased compared to regular photoinitiators which makes CARs especially interesting for sub-0.5-µm lithography.

In this work, various low molecular weight, glass-forming CAR components were investigated with regard to film formation by physical vapor deposition. The researched CAR systems consist each of a molecule with several phenolic groups, an acid labile crosslinker (*N*,*N*,*N*,*N*-tetra(methoxymethyl)glycoluril, "Powderlink®") and a PAG.
In the group of Prof. Dr. Christopher Ober at Cornell University, wetchemical investigations were performed with several low molecular weight CAR systems, amongst others one which consists of 1,1,1-tris(4-hydroxyphenyl)-1-ethyl-4-isopropylbenzene ("trisphenol"), Powderlink® and the ionic PAG triphenylsulfonium triflate. This CAR system was the starting point for the herein performed PVD investigations.

In the field of photolithography, ionic PAGs are normally preferred to non-ionic PAGs because of their higher efficiency (see Chapter 1.3). Since ionic PAGs cannot be evaporated, non-ionic PAGs were investigated in this thesis to replace the ionic PAG. The requirements included thermal stability, the perpetuation of the amorphous phase of the photoresist film and sufficient interactions towards the substrate when depositing in high vacuum. Regarding the above mentioned trisphenol photoresist system, 2-(4-methoxystyryl)-4,6-bis-(trichloromethyl)-1,3,5-triazine ("triazine") and tetrabromobisphenol A ("TBBPA") were both found to be adequate replacements; structures could be produced by subsequent exposure and development of the CAR systems. Triazine turned out to be more suitable for PVD processing because of its steady evaporation and deposition behavior. Thus, it was the first non-ionic PAG of choice, and employed with the above stated trisphenol system for solvent-free film preparation and combinatorial experiments (see Ch. 3.1).

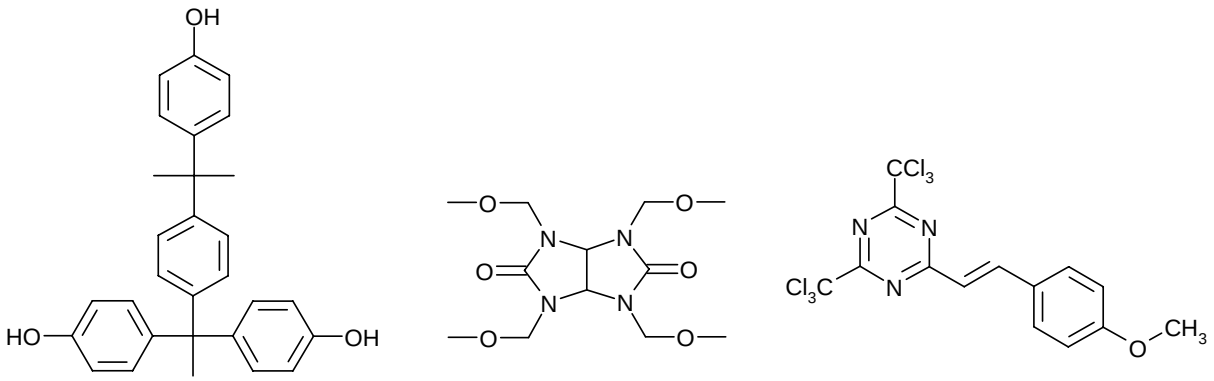
Since the HCl acid molecules, which are generated from triazine when irradiated, diffuse excessively because of their small size, reactions in the adjacent non-exposed areas can be additionally initiated. This circumstance has a negative impact on resolution and line edge roughness (LER) of the produced features. Thus, a different non-ionic PAG with a larger acidid moiety was additionally investigated for PVD suitability. *N*-Hydroxynaphthalimide triflate exhibits a similar UV absorption spectrum as triazine and shaped up as being also well suitable for PVD. It was employed with two other CAR systems. Trisphenol was replaced for materials containing four phenolic groups instead of its three: 6,6',7,7'-tetrahydroxy-4,4,4',4'-tetramethyl-2,2'-spirobichroman ("spirobichroman"), or 5,5',6,6'-tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-spirobisindane ("spirobisindane") (see Ch. 3.2). Powderlink® remained as crosslinker in all three investigated CARs.

Cross experiments in which triflate served as PAG in the triflate CAR and triazine served as PAG in the spirobichromane CAR gave no satisfying outcome, the resulting features showed no or only very fringy, non-continuous lines.

To determine the actual wt.% composition on the substrates, different measurements were first performed with IR and NMR spectroscopy. It was found that IR spectra of three different substances are too complex for quantitative interpretation, whilst the sample amount prepared by PVD is too small for the employed NMR equipment. HPLC analysis turned out to be a highly suitable detection method for evaporated material regarding qualitative (for confirming the thermal stability of the substances by recording chromatograms before and after single evaporation) as well as quantitative analysis (by establishing a calibration which relates to the film thicknesses measured by the sensors near the sources).

3.1 Physical Vapor Deposition of Molecular Glass Photoresists: A New Route to Chemically Amplified Patterning (Publication: Appendix A1)

In publication A1, a molecular glass photoresist system consisting of three substances is investigated for its suitability for PVD application, and the optimization of composition and exposure dose utilizing combinatorial techniques. The employed substances are shown in Figure 3-1, first the main component 1,1,1-tris(4-hydroxyphenyl)-1-ethyl-4-isopropylbenzene ("trisphenol") **1**, second an acid labile crosslinker *N*,*N*,*N*,*N*-tetra(methoxymethyl)glycoluril ("Powderlink®") **2**, and third a non-ionic photoacid generator (PAG) 2-(4-methoxystyryl)-4,6-bis-(trichloromethyl)-1,3,5-triazine ("triazine") **3**.



1 **2** **3**

Figure 3-1. Chemical structure of the three components in the investigated photoresist system. 1,1,1-tris(4-hydroxyphenyl)-1-ethyl-4-isopropylbenzene ("trisphenol") **1**, acid labile crosslinker *N,N,N,N*-tetra(methoxymethyl)glycoluril ("Powderlink®") **2**, and photoacid generator (PAG) 2-(4-methoxystyryl)-4,6-bis-(trichloromethyl)-1,3,5-triazine ("triazine") **3** (numbering according to A1).

Components **1** and **2** have already been successfully established as CAR compounds together with ionic PAGs by Ober et al.[48] Because of their salty character, ionic PAGs cannot be employed in evaporation processes, though. To adopt this specific CAR system to PVD, the normally used PAG triphenylsulfonium triflate had to be replaced by a vapor-depositable PAG. After several investigations, non-ionic PAG triazine **3** emerged as the most suitable replacement; amorphous films of the three substances could be prepared by coevaporation. By analyzing samples from each of the substances before and after single vapor deposition by

high pressure liquid chromatography (HPLC), the thermal stability of each of the components was confirmed. However, before evaporation, the quartz tube of trisphenol has to be emptied and refilled each time with fresh material since trisphenol that is heated for several times decomposes to some extent into a bisphenol with a double bond. This molecule was detected as a second peak from vapor-deposited trisphenol, its identity was confirmed by UPLC/MS (MS^2) measurements.

To optimize the composition of the photoresist, ten sectors (a sector library) with different compositions of **1**, **2**, and **3** were prepared by PVD onto an unprimed Si wafer using combinatorial mask techniques (see Table 3-1).

Table 3-1. Combinatorial library for optimizing the composition of the photoresist. Different compositions of Powderlink®, trisphenol and PAG triazine in the ten sectors (A to J) on the silicon wafer were prepared. The ratios were calculated by an HPLC calibration which provided a correlation between evaporation rates and composition. From sector A to E, the evaporation rate—and thus the wt.%—of trisphenol, and from sector F to J the evaporation rate of triazine was increased.

sector	Powderlink® on wafer [wt.%]	Trisphenol on wafer [wt.%]	PAG on wafer [wt.%]
A	32.6	67.3	0.1
B	24.4	73.8	1.8
C	12.6	86.7	0.7
D	7.2	92.7	0.1
E	3.9	96.0	0.1
F	14.9	84.7	0.4
G	14.9	84.4	0.7
H	15.1	83.3	1.6
I	14.0	82.0	4.0
J	12.8	80.6	6.6

Then, each of the produced ten sectors was irradiated with six different exposure doses of 40, 240, 440, 640, 840, and 1040 mJ/cm^2 at 365 nm. By this, at the total sixty spots with differing compositions and exposure doses were combinatorially created on the same wafer. After a post exposure bake (PEB) for 30 s at 90 °C, the substrate was developed with tetramethylammonium hydroxide (TMAH) solution. The unexposed material was soluble in aqueous basic solution, so, after development, negative tone patterns were received. Since in a

preliminary test, the normally used concentration of 0.26 N TMAH removed not only the unexposed, but all material, the developer was used with a dilution of 1:27 (0.26 N TMAH:deionized water).

For investigating the composition on the substrates, HPLC calibrations of the separately evaporated substances, relating the measured film thicknesses to the amounts, were performed foremost. The actual composition in the sectors was then determined by measuring the film thicknesses of each of the components with quartz sensors when evaporating. It was found that even though the stoichiometric relation of **1** and **2** is about 1.6:1, the optimized composition is about 7:1 with 86.7wt.% trisphenol, 12.6wt.% Powderlink® and 0.7wt.% PAG triazine (sector C3). The optimized pattern of this composition was achieved with an exposure dose of 440 mW/cm^2 (see Fig. 3-2).

Figure 3-2. Reflection microscope images taken for the optimization of the composition. The optimized sector C3 after PEB and development. The white lines are the exposed parts, the darker area is the surface of the silicon wafer. The numbers indicate the linewidth in microns. The optimized composition of 12.6wt.% Powderlink®, 86.7wt.% trisphenol and 0.7wt.% PAG triazine was exposed to a dose of 440 mJ cm^{-2} at 365 nm and baked at 90^{o}C for 30 s. After patterning, the wafer was dipped into a diluted TMAH solution (1:27 (0.26 N TMAH:deionized water)) for 6 seconds, and rinsed with deionized water afterwards. No residues can be observed.

In a different experiment, the developing time and dilution was optimized. A film with the above described optimized composition was prepared by PVD on one unprimed silica wafer. Then it was exposed to 440 J/cm^2 and postbaked for 30 s at 90 °C. The wafer was cut into small pieces. These pieces were dipped into various dilutions of TMAH, ranging from undiluted 0.26 N aqueous TMAH to a 1:200 (0.26 N TMAH:deionized water) solution for defined times (ranging from 1 s to 600 s). The resulting features were observed with optical and scanning electron microscopy (SEM). By these experiments, it was confirmed that undiluted 0.26 N TMAH solution removes the complete resist film. Using a dilution of 1:200 resulted in no patterns at all: no material was removed, regardless the time (a maximum of

15 min was investigated). The optimized results with clear lines and no residues were found with a dilution of 1:20 to 1:50 (see Fig. 3-3, developed with a dilution of 1:40).

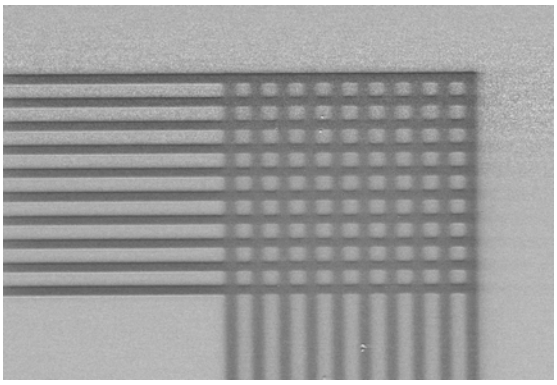


Figure 3-3. SEM image taken for the optimization of the dilution of the developing TMAH solution. The optimized sector C3 after PEB and development. The dark lines are the exposed parts, the lighter area is the surface of the silicon wafer. The optimized composition of 12.6wt.% Powderlink®, 86.7wt.% trisphenol and 0.7wt.% PAG triazine was exposed to a dose of 440 mJ cm^{-2} at 365 nm and baked at 90°C for 30 s. After patterning, the wafer was dipped into a diluted TMAH solution (1:40 (0.26 N TMAH:deionized water)) for 13 seconds, then rinsed with deionized water afterwards. The features are sharp, and no residues can be observed.

In summary, a CAR system could be successfully prepared by PVD, separated lines of 700 nm were observed. This solvent-free film fabrication method allowed a high throughput approach to optimize the composition and the exposure dose for this specific photoresist. The development was also optimized in respect of dilution of the TMAH solution and time of development. HPLC could be established as a suitable detection method for the thermal stability of the used materials and for quantifying the composition in the prepared sectors.

3.2 Towards Environmentally Friendly, Dry Deposited, Water Developable Molecular Glass Photoresists (Publication: Appendix A2)

A chemically amplified molecular glass photoresist consisting of a molecule with three phenolic groups, the crosslinker Powderlink® and a non-ionic PAG could be prepared by PVD and optimized by combinatorial approaches in publication A1. For publication A2, two further photoresists with the same reaction mechanism were examined, improvements regarding development and resolution were achieved. Powderlink® **3** remained as acid labile crosslinker. The formerly used non-ionic PAG triazine was substituted by *N*-hydroxynaphthalimide triflate ("triflate") **4**. As main component, either 5,5',6,6'-tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-spirobisindane ("spirobisindane") **1,** or 6,6',7,7'-

tetrahydroxy-4,4,4',4'-tetramethyl-2,2'-spirobichroman ("spirobichroman") **2** were employed (see Fig. 3-4) to replace trisphenol.

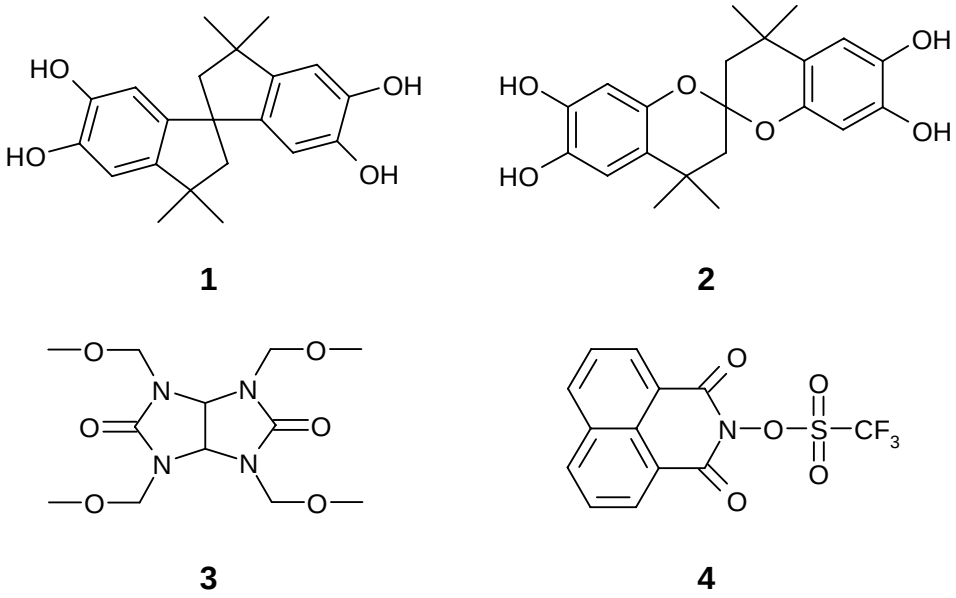


Figure 3-4. Chemical structure of the four components in the investigated photoresist systems. 5,5',6,6'-tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-spirobisindane ("spirobisindane") **1** or 6,6',7,7'-tetrahydroxy-4,4,4',4'-tetramethyl-2,2'-spirobichroman ("spirobichroman") **2**, acid labile crosslinker *N,N,N,N*-tetra(methoxymethyl)glycoluril ("Powderlink®") **3** and non-ionic PAG *N*-hydroxynaphthalimide triflate ("triflate") **4** (numbering according to A2).

The PAG triazine used in A1 produces a very small, mobile molecule when irradiated, hydrochloric acid. PAGs with a larger acidic group and a smaller diffusion propensity are preferred as components in CARs, though. A very common moiety in this research field is that of triflate (trifluorosulfonic) moiety. The generated triflate acid, sometimes also called triflic acid, is first a very strong acid and second significantly larger than HCl. To improve the resolution obtained in A1, a vapor-depositable, non-ionic PAG with a triflate moiety is supposed to replace triazine. This substitution was found in *N*-hydroxynaphthalimide triflate ("triflate") **4**.

The three-phenolic main component trisphenol from A1 was replaced in A2 with four-phenolic compounds spirobisindane **1**, and spirobichroman **2**, respectively. Low molecular weight molecules with spiro functionalities are known for their glass-forming properties and thus promising candidates for amorphous photoresist components. This assumption was confirmed by evaporating mixtures of **1**,**3**,**4**, and **2**,**3**,**4**, respectively, which both gave transparent, glass-like films.

All substances were investigated for their thermal stability by recording the associating HPLC chromatograms before and after separate evaporation. Regarding **3** and **4**, no differences were

detected meaning that they do not undergo thermal decomposition. Looking at the chromatograms of the spiro compounds **1** and **2**, though, in both cases a time-dependent second peak appeared. The longer the dissolved sample remained in the HPLC sample vial—*regardless if taken before or after evaporation*—the larger the unknown second peak became. It was assumed that an autoxidation of the spiro compounds took place. To prevent this, the effect of several antioxidation reagents was tested by adding a small amount to dissolved samples of **1**, and **2**. Ascorbic acid finally inhibited the reaction successfully. Even after several days, the second peak was not found. Thus, deionized water with a small amount of ascorbic acid was utilized for the solution mixture with acetonitrile to rinse off the evaporated and deposited test wafer pieces. Since ascorbic acid and Powderlink® show a similar retention time in the standard mobile phase (60vol% acetonitrile, 40vol% water) under the applied HPLC conditions, a mobile phase gradient was developed and employed to separate these two peaks. After this method optimization was successfully established, evaporated samples of both the spiro compounds were proven to not thermally degrade under the used PVD conditions.

As in A1, the composition of the photoresists was optimized by producing a sector library of ten sectors with different compositions on the same wafer. This was performed with **1**,**3**, and **4** as well as with **2**,**3**, and **4**. Each of the sectors on the resulting wafers was then exposed to six different UV doses (**1,3,4**: 70, 175, 280, 385, 490, and 595 mJ/cm²; **2,3,4**: 280, 420, 560, 700, and 840 mJ/cm²) at 365 nm. At the total, sixty spots with different compositions and exposure doses were fabricated of each spiro photoresist on the same wafer. Different post exposure bake (PEB) temperatures (90, 100, 110, and 120 °C, each for 30 s) were investigated for the spirobichroman photoresist. With higher temperatures, the necessary exposure dose for the general producement of patterns decreased, but the line sharpness was reduced. Thus, PEB was performed at 90 °C for 30 s, which are the same PEB parameters as used in A1.

As it was found in prescreening experiments, both photoresist systems could be developed with pure, deionized water with a development time of about 30 s. This makes the development very simple, since unlike the photoresist in A1, the developer dilution does not have to be optimized. Additionally, it reduces costs and waste.

The resulting patterns were observed with reflection microscope. Feature sizes as small as 400 nm (the smallest lines on the applied mask) could be produced. The optimized features from spirobisindane were obtained with a composition of 79.9wt.% spirobisindane, 17.3wt.% Powderlink®, and 2.8wt.% triflate, exposed to a dose of 385 mJ/cm² at 365 nm. The optimized features from spirobichroman were obtained with a composition of 77.6wt.% spirobichroman,

20.2wt.% Powderlink®, and 2.2wt.% triflate, exposed to a dose of 840 mJ/cm² at 365 nm (see Fig. 3-5).

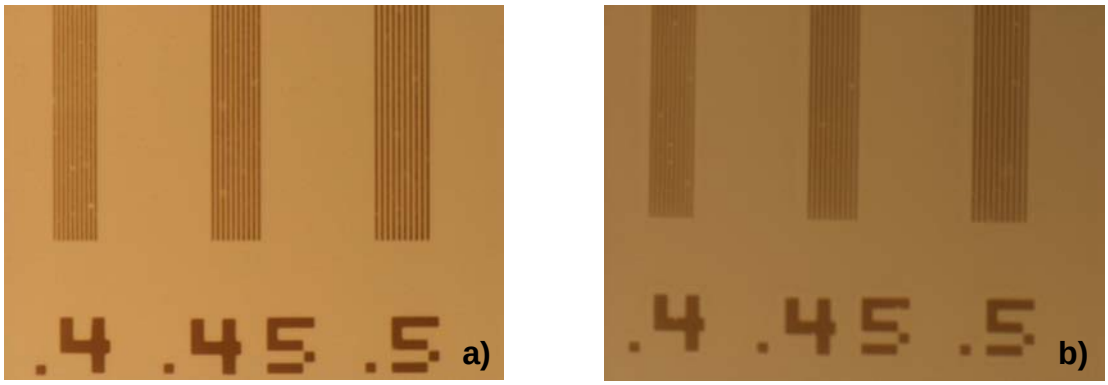


Figure 3-5. Reflection microscope image (darker parts were exposed) of the optimized compositions of a) spirobisindane photoresist (sector F in Table 1). The optimized composition of 79.9wt.% spirobisindane, 17.3wt.% Powderlink®, and 2.8wt.% triflate was exposed to a dose of 385 mJ/cm² at 365 nm. After exposure and performing a PEB at 90 °C for 30 s, the wafer was dipped into deionized water for development.
b) the spirobichroman photoresist. The optimized composition of 77.6wt.% spirobichroman, 20.2wt.% Powderlink®, and 2.2wt.% triflate was exposed to a dose of 840 mJ/cm² at 365 nm. After exposure and performing a post exposure bake (PEB) at 90 °C for 30 s, the wafer was dipped into deionized water for development.

4. GLASS-LIKE SELF-REACTING COUMARIN DERIVATIVES

The second photoresist type investigated in this thesis is dealing with newly synthesized, low molecular weight coumarin derivatives. Coumarin and many of its derivatives are known for undergoing a [2+2] photodimerization when exposed to wavelengths above 300 nm (see Ch. 1.5 and Fig. 4-1). This makes them promising candidates for photolithography purposes.

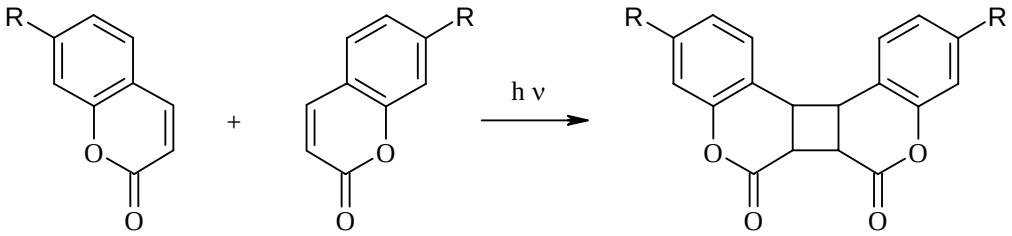


Figure 4-1. Schematic sketch of the photodimerization reaction of coumarin and its derivatives. When exposed to UV light, two coumarin functional groups undergo a [2+2] cycloaddition by cleavage of their double bounds to form a dimer.

Thus, unlike the chemically amplified resists which were introduced in Chapter 3 and consisted of three substances, the herein presented photoresists get by with only one component, a coumarin derivative. To improve the photolithography process and reduce the exposure time, the coevaporation with a sensitizer was also investigated in this thesis.

4.1 Synthesis and All-Dry Lithography of Glass-Like Coumarin Derivatives (Manuscript: Appendix A3)

The focus of the work described in publication manuscript A3 lied on the synthesis of glass-forming coumarin derivatives and their application as vapor-depositable, low molecular weight photoresists. Not only the film formation was performed solvent freely by physical vapor deposition (PVD) as described in A1 and A2, but also the development.

First, suitable coumarin derivatives had to be synthesized; the desired properties of the products were given from their designated application as thermally stable and glass-forming. 7-Hydroxycoumarin and various acids, depending on the desired “core” of the ester, served as

starting materials for coumarin esters. Standard esterification methods like the use of suitable alcohol and acid chloride molecules in the presence of pyridine failed or gave product mixtures which where too complex to separate, though. After several unsuccessful synthesis attempts, a convenient method was found in water-soluble 1-(3-dimethylaminopropyl-)-3-ethylcarbodiimide hydrochloride (EDAC) which served as esterification agent, and in dimethyl aminopyridine (DMAP) as a catalyst. With regard to the desired glass-forming property, the synthesis focused on asymmetric molecules, the use of non-planar educts or the introduction of bulky groups. The precipitated hydrophobic ester products were filtrated, while the excessive 7-hydroxycumarin and the resulting urea, which was generated in the reaction, could be removed by rinsing the product with acidic water. This method gave yields in the range of 40 to 85%. Nine different coumarin esters, as illustrated in Figure 4-2, were synthesized in respect to the above stated requirements.

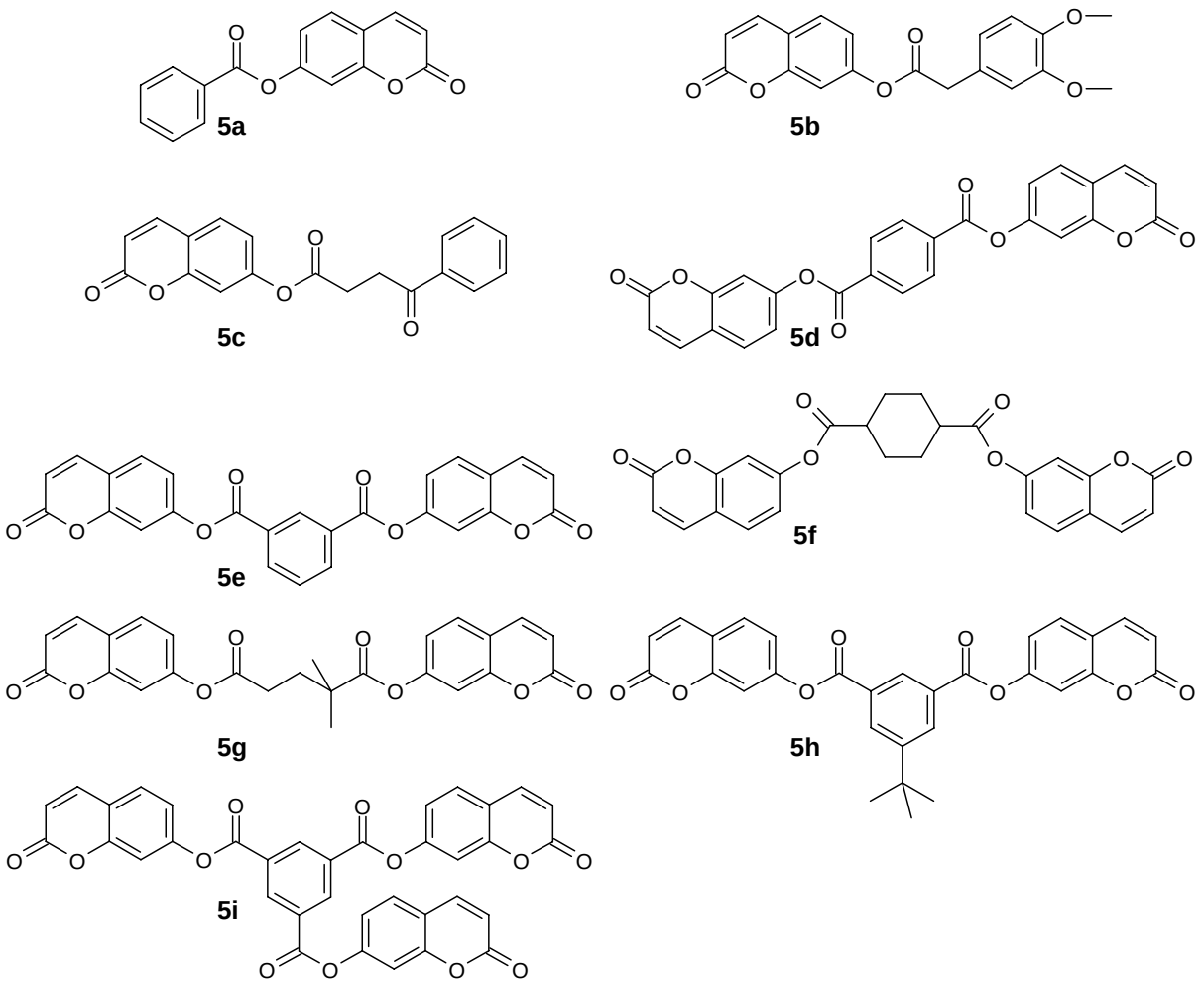


Figure 4-2. Overview of the nine different coumarin esters which were synthesized in order to obtain vapor-depositable, glass-forming photoresist material (numbering according to A3).

After characterizing the substances by NMR spectroscopy, elementary analysis, and HRMS, their thermal characteristics were investigated by DSC and TGA. **5b**, **5g** and **5h** showed a glass-transition temperature T_g: **5b** at 15 °C, **5g** at 25 °C, and **5h** at 88 °C, which proved an amorphous phase. As preliminary tests for vapor deposition, each of the materials was sublimed. The sublimation was successful for derivatives **5a**, **5b**, **5d**, **5e**, **5g**, and **5h**. Thermal decomposition was observed with **5c**, **5f**, and **5i**. Thus, these materials were not suitable for PVD and not further tested. The sublimable esters were vapor-deposited to investigate their film-building qualities. With **5a**, no material was found on the substrate after evaporation in high vacuum. The interaction between the substance and the surface is supposedly too weak under the applied conditions (substrate at room temperature) so that desorption takes place. Crystalline films were formed by **5b**, **5e**, and **5g**. An amorphous film which is at least stable for two weeks (evaporated onto a quartz plate and observed under polarization microscope) could be fabricated with coumarin ester **5h**. Additionally, a coevaporation of **5g** and **5h** was tested. The produced film was amorphous first, but started to crystallize about 2 hours after deposition. Thus, investigations in regard to an all-dry photoresist focused on **5h** alone.

To determine the necessary exposure time, a film of **5h** with a thickness of about 300 nm was prepared by PVD on a quartz plate. The absorption spectra before and after irradiation (wavelength range 330 to 480 nm, exposure dose 40 mJ/cm^2) at defined spots for specified times from 5 to 50 min was measured. The decrease of the two maxima, which relate to the double bound of the monomer at 280 and 315 nm, in dependence of the exposure time, indicates the successful photoreaction of the molecules (Fig. 4-3).

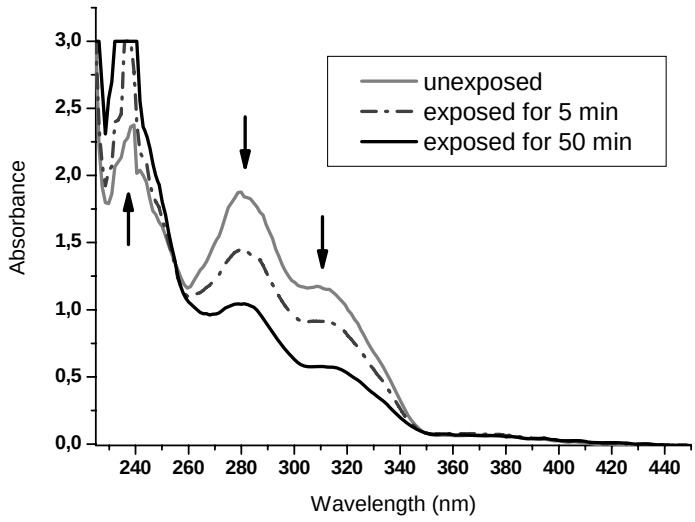


Figure 4-3. The decrease of the two maxima at 280 and 315 nm by an increasing exposure time indicates the photoreaction of the coumarin derivative.

The reason for the long exposure time is the little overlapping of the absorption spectra of the coumarin derivative and the spectra of the employed UV lamp. Since the photoproducts would preferably reform to the monomers when irradiated with wavelengths smaller than 300 nm, the long exposure times could not be avoided under these conditions. Deducting from the previous described UV absorption measurements on quartz glass, the exposure time for the following patterning experiments was set to 50 min.

To produce features, a film of **5h** was deposited by PVD onto a silica wafer with a thickness of about 150 nm. The wafer was exposed for 50 min through a mask which provided lines from 1 to 10 µm. To develope the features dryly, a hollow, high vacuum facility was build. One half of this metal chamber was put on a precision hot stage, the other half was cooled by standing on a brass block which was situated in an ice bath. The wafer, which had been exposed via a mask aligner through the mask, was broken into small pieces. One piece was situated into the cooled part of the development equipment at a time. Vacuum was applied and the hot stage was set to a defined temperature. After the vacuum and the temperature were stable, the wafer piece was slid into the heated part by tilting the facility. After a defined time, the piece was slid back into the cooler part. Various times from 1 min to 15 h and temperatures from 80 to 320 °C were each investigated with different wafer pieces. The resulting patterns were observed with reflection microscope. It was found that features could be obtained by this all-dry photolithography process. Optimized development conditions were determined to be 15 h at 120 °C. The resulting lines were continuous and showed no residues in the smaller areas, though crystals could be observed in larger unexposed areas (Fig. 4-4). Monomers of the coumarin derivative did not evaporate from these larger areas as desired, but crystallized.

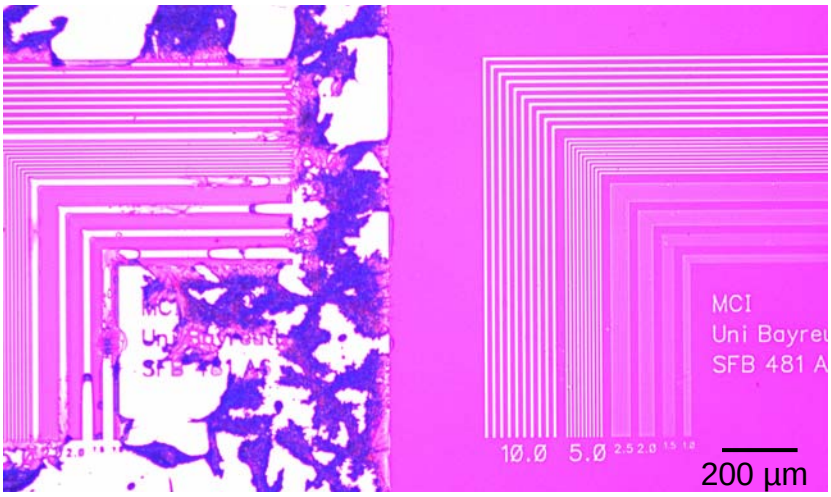
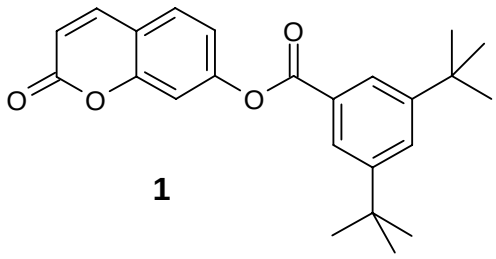


Figure 4-4. Patterns can be obtained by an all-dry photolithography process using a low molecular weight coumarin derivative as resist material (light parts are the wafer surface). No residues can be observed on the right. In larger areas, crystals remain in the unexposed parts, though.

4.2 All-Dry Processing of a Negative Tone Photoresist based on a Low Molecular Weight Coumarin Derivative (Manuscript: Appendix A4)

In publication manuscript A3, the general suitability of a coumarin ester for an all-dry low molecular weight photolithography was proven. Small features could be produced without the use of any solvents. Still, some issues like a long exposure time and crystallization to some extent after development were existent, which are investigated in this manuscript. When developing the pattern by thermal treatment under high vacuum, the monomers of the most successful material of publication manuscript A3 showed crystallization in larger unexposed areas of the resist instead of evaporation. Thus, the focus of this work lied on the synthesis of a smaller derivative with a decreased tendency to crystallize in the development step and which would thus evaporate better. Instead of bifunctional molecules (see Ch. 4.1) which result in a chain when irradiated, a smaller, monofunctional coumarin derivative was synthesized (see Fig. 4-5).

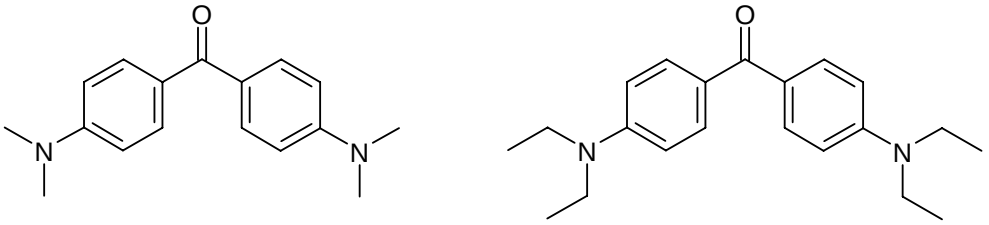


1

Figure 4-5. Schematic sketch of the monofunctional coumarin derivative which was newly synthesized (numbering according to A4).

When deposited by PVD onto quartz and silica plates, the generated films were amorphous. DSC analysis showed a T_g of 33 °C and a T_m of 134 °C. To identify the necessary exposure dose, the same procedure as described in A3 was performed: The derivative was evaporated onto a quartz plate, and certain spots were exposed to defined times of irradiation. The UV spectra before and after exposure were measured and analyzed. As in A3, 50 min of exposure time were necessary to obtain an explicit decrease in the two maxima at 280 and 315 nm which relate to the double bond. The reason for the long exposure time is given in Chapters 1.5 and 4.1. The coevaporation of a sensitizer was considered to decrease the necessary exposure time. Sensitizers are successfully employed with dissolved coumarin derivatives and with photoresists containing cinnamic acid derivatives, a functional group related to that of

coumarin. The requirements for a sensitizer used in all-dry lithography such as thermal stability and glass-forming ability limit the number of suitable agents. Except for benzophenone which has a low melting point and is thus not suitable for PVD, all literature-mentioned sensitizers are toxic and cancerous, like Michler's ketone **2a** (Fig. 4-6) which is one of the most effective literature-known sensitizers for cinnamic acid derivatives.[35] A very similar molecule which was not listed as sensitizer, Michler's ethylketone **2b**, is less harmful. Thus, this substance was chosen for investigations regarding its suitability for PVD, glass-forming and sensitizing properties by coevaporating it with the above described coumarin derivative **1** in a wt.% relation of about 1:9 on quartz plates.



2a **2b**

Figure 4-6. Schematic sketch of sensitizer Michler's ketone **2a** and Michler's ethyl ketone **2b** (numbering according to A4).

The produced films were about 300 nm thick and amorphous. The UV spectrum measurement of the sensitized film of **1** showed an extended absorption spectrum towards longer wavelengths (Fig. 4-7) and is thus an improvement in a higher overlapping with the UV spectrum of the employed lamp. As in A3, certain spots were exposed to defined times. After 5 min of irradiation, the spectra of the sensitized film resembled that of the unsensitized film when exposed to 50 min (Fig. 4-3 in Ch. 4.1). Thus, the exposure dose which was necessary for a sufficient reaction rate, i.e. a significant decrease of the two described maxima, was clearly reduced which implied that **2b** showed the desired sensitizing properties regarding **1**.

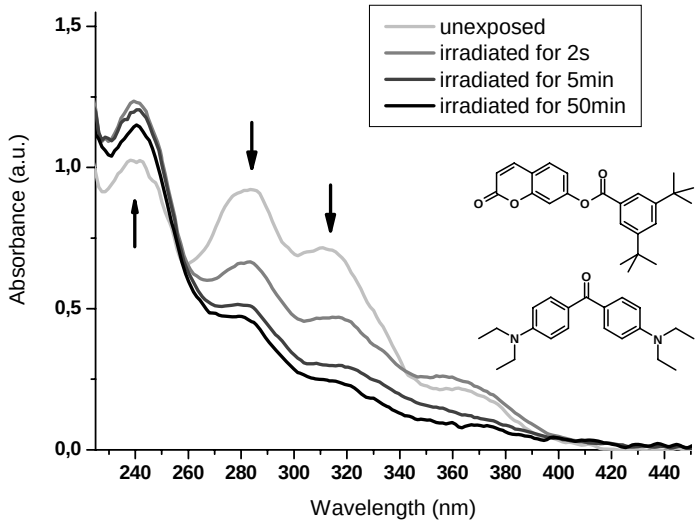


Figure 4-7. UV spectra of **1** and the sensitizer Michler's ethyl ketone **2b**, coevaporated onto a quartz plate (film thicknesses about 300 nm): unexposed (light grey line), irradiated for 2 s (medium grey line), 5 min (darker grey line) and 50min (black line), respectively. Both maxima at about 280 and 315 nm, which correspond to the double bound of the monomer, decrease by time of irradiation indicating that the cleavage of the double bond to form a cyclobutane ring takes place. The extended spectrum from 340 to 400 nm is due to the sensitizer **2b** which increase the overlap regarding the UV spectrum of the employed lamp (330 – 480 nm).

After the effectiveness of a coevaporation of sensitizer **2b** with **1** was confirmed, the materials were coevaporated onto silica wafers to produce thin films for pattern creation. The film thickness varied from 25 to 90 nm. For investigating the influence of **2b** on parameters and created features, **1** was additionally vapor-deposited separately. Films of **1** were exposed through a mask (linewidths from 1 to 10 µm) to 5 and 50 min. Deriving suitable exposure times for films of **1** and **2b** from the results of the UV spectra measurements, films of the coevaporated materials were irradiated for 10 s and 5 min. The dry development, in which the monomers in the unexposed areas were supposed to evaporate, was performed in the same small vacuum chamber as described in Chapter 4.1. The development temperatures varied from 70 to 100 °C. It was found that below 70 °C, the monomers would not evaporate, and above 100 °C, the exposed parts of the resist film started to melt. Development times varied from 30 min to 15 h. The resulting patterns were observed by optical microscopy. No crystals or other residues were detected which implied that the photoresist material could be improved. When comparing the features received from **1** to those received from the mixture of **1** and **2b**, both exposed to 5 min and developed at 80 °C for 15 min in high vacuum, the influence of the sensitizer on the exposure dose was clearly proven. While the patterns from **1**

did not show separated lines, continuous, sharp features were received from the coevaporated mixture. These results were found from **1** only after 50 min exposure time. A further reduction in the exposure time of the mixture resist was not successful. Even though the UV spectrum of **1** and **2b** showed a significant decrease of the double bound maxima already after 2 s of irradiation (see Fig. 4-7), it was found that an exposure time of 10 s is too short to produce continuous lines.

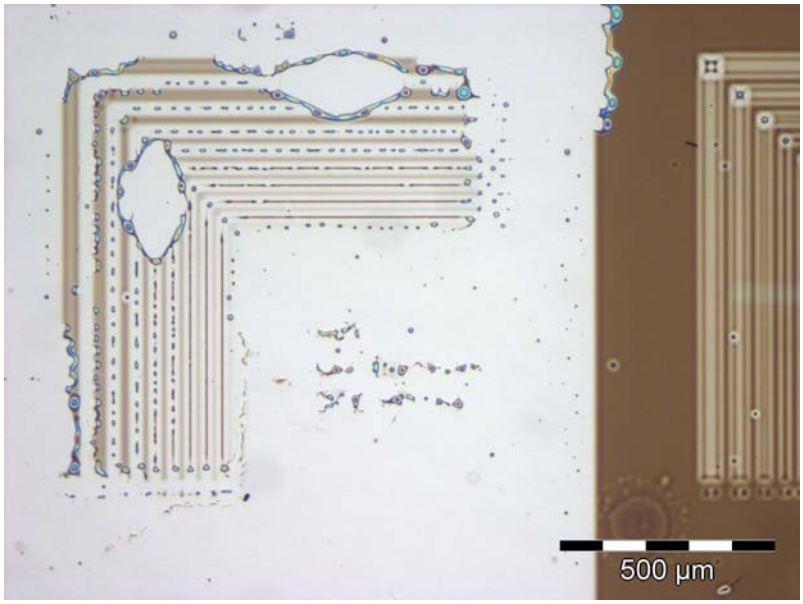


Figure 4-8. An 80 nm thick film of **1** and **2b** (relation 1:9), exposed to 10 s and developed at 80 °C for 15h (dark areas were exposed).

Additionally, a dependency on the film thickness was observed: Whilst a 25 nm thick film of the coevaporated mixture gave continuous, sharp features (see Fig. 4-9), an 80 nm thick film which was processed under the same conditions showed melted lines. The film thickness seems to influence the glass transition temperature of the mixture of **1** and **2b** and is thus of high importance for the quality of the features.

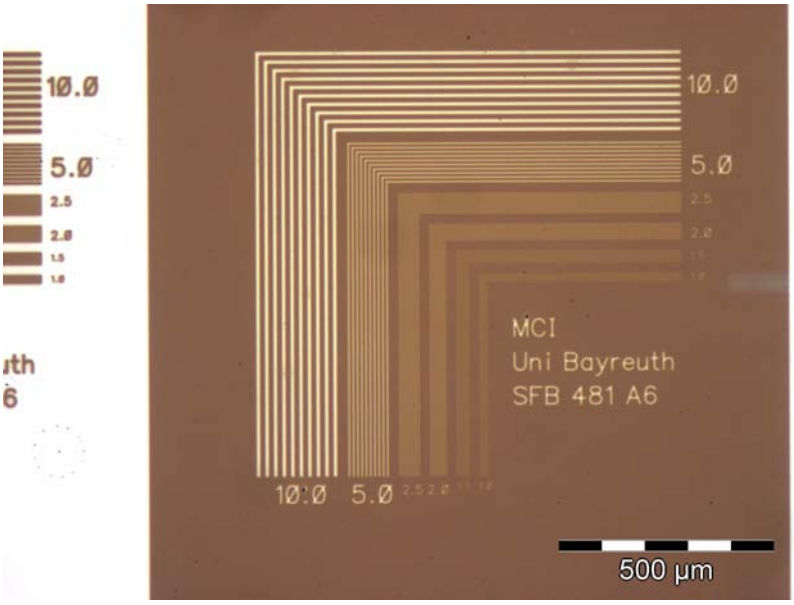


Figure 4-9. A 25 nm thick film of 1 and 2b (relation 1:9), exposed to 5 min and developed at 85 °C for 60h (dark areas were exposed).

In summary, it can be said that in publication manuscript A4, the development step of an all-dry photolithography process based upon coumarin derivatives could be clearly improved in comparison to publication manuscript A3. A new coumarin derivative was synthesized which gave no residual crystals when evaporated. Additionally, the necessary exposure could be significantly decreased. By coevaporating sensitizer **2b** with coumarin derivative **1**, the exposure time could be reduced from 50 min to 5 min. The produced features from **1** and from a mixture of **1** and **2b** did not differ in quality, but only in the necessary exposure time.

5. SUMMARY

This thesis is concerned with solvent-free film preparation of low molecular weight, amorphous, photosensitive resists by physical vapor deposition (PVD), their subsequent UV exposure through a mask and their development to produce features in the micro- and nanometer range. These process steps are the basis for photolithography. By using a mask, not the complete photosensitive film is irradiated, but only certain areas. Chemical reactions are initiated in the exposed areas which influence physical properties of the resist material, e.g. its solubility in solvents. In the final step, the development, the generated difference is exploited by either removing the exposed parts (*positive tone resist*) or the unexposed parts (*negative tone resist*).

In the frame of the thesis towards a solvent-free lithography, the combinatorial PVD techniques developed in our group allow the preparation of gradients or sectors on the same substrate as well as the coevaporation of several substances. By the employment of three effusion heating sources and five quartz sensors, which individually measure evaporation rates and layer thicknesses, organic materials can be evaporated in high vacuum with an exact ratio and film thickness. Whilst evaporation, different masks can be positioned between the sources and just below the substrate so that the material deposit only within defined sectors of the substrate. These masks and the adjustment of the source temperature—and thus an alteration of the evaporation rate—allow the combinatorial preparation of a so-called sector library with various sectors with different compositions on the same substrate, and in one sequence without breaking the vacuum or opening the PVD chamber.

In the thesis, two types of low molecular weight, negative tone photoresists were investigated:

(1) Research was carried out on *molecular glass photoresists* which consist of several components. One of these components, a photoacid generator (PAG), generates acid molecules when exposed to suitable wavelengths. In a post-exposure bake, the formed protons catalytically initiate reactions between the other resist components (chemical amplification).

(2) Newly synthesized, self-reactive *coumarin derivatives* were explored in regard to their suitability for an *all-dry photolithography process*. Additionally, the reduction of the exposure time by employing a vapor-depositable sensitizer was achieved.

(1) Physical vapor deposition of molecular glass photoresists as a new route to chemically amplified patterning: Investigations and characterizations (DSC, TGA, HPLC) were performed on the suitability of various low molecular weight chemically amplified resist (CAR) materials for film deposition via PVD as well as subsequent photolithography processes. Three ternary systems (**i**, **ii**, and **iii**) were identified to accomplish the requirements (vapor depositability, formation of glassy films, photostructurability). Each of them consists of a molecule with several phenolic groups, an acid labile crosslinker (*N*,*N*,*N*,*N*-tetra(methoxymethyl)glycoluril, trade name "Powderlink®"), and a PAG:

- **i.** 1,1,1-tris(4-hydroxyphenyl)-1-ethyl-4-isopropylbenzene ("trisphenol"), Powderlink®, and the non-ionic PAG 2-(4-methoxystyryl)-4,6-bis-(trichloromethyl)-1,3,5-triazine ("triazine")
- **ii.** 5,5',6,6'-tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-spirobisindane ("spirobisindane"), Powderlink®, and the non-ionic PAG *N*-hydroxynaphthalimide triflate ("triflate")
- **iii.** 6,6',7,7'-tetrahydroxy-4,4,4',4'-tetramethyl-2,2'-spirobichroman ("spirobichroman"), Powderlink®, and the non-ionic PAG *N*-hydroxynaphthalimide triflate ("triflate")

By utilizing the combinatorial mask technique of the PVD facility, sector libraries were prepared to optimize the composition of each of the CARs. The exposure dose was combinatorially optimized by irradiating each of the created sectors with different doses of 365 nm UV light. Additionally, the development was optimized by investigating several dilutions of the developer tetramethylammonium hydroxide (TMAH) and various development times. Interestingly, it was found that the resists **ii** and **iii** can be developed with pure water which is a step towards more environmentally friendly processes. With the employed equipment, features with a resolution of about 700 nm (**i**), and 400 nm (**ii**, and **iii**) could be realized. The resulting patterns were observed with optical and scanning electron microscopy (SEM) to determine line qualities and thus the optimized compositions and exposure doses for the three investigated CARs. HPLC analysis turned out to be well suitable for detecting small amounts of evaporated material and was thus utilized to determine the thermal stability of investigated substances and the compositions in the prepared sectors.

(2) Synthesis and all-dry lithography based upon low molecular weight coumarin derivatives: The second photoresist type which was investigated in this thesis is based upon self-reactive coumarin derivatives. When exposed to wavelengths above 300 nm, many undergo a [2+2] cycloaddition. Depending on the number of functional coumarin groups, dimers, chains, or

networks can be generated by this photoreaction. The ten coumarin esters presented in this thesis were, except for one, newly synthesized and characterized by NMR spectroscopy, HRMS, elemental analysis, DSC, and TGA. They were synthesized in respect of requirements regarding photoresists and PVD, e.g. glass-forming properties, and thermal stability. Several of the synthesized esters could be evaporated without decomposition. Two esters, 1,3-dibenzoic-5-tert-butylcoumarinester und 3,5-di-tert-butylbenzoiccoumarinester, produced amorphous and thus transparent films which are required for an employment as photoresists. Since the monomers preferably reform when the irradiated product is exposed to wavelengths below 300 nm, irradiation only above this critical wavelength was employed. This circumstance lead to long exposure times of 50 min because of the small overlap between the absorption spectra of the coumarin derivatives and that of the lamp. The successful employment of a sensitizer, Michler's ethyl ketone, which could be coevaporated with 3,5-di-tert-butylbenzoiccoumarinester, reduced the necessary exposure dose significantly from 50 to 5 min (tracked by UV spectroscopy).

Since the above described coumarin derivative monomers evaporate in high vacuum, a dry development through the removal of the unexposed monomers by thermal treatment under high vacuum in a self-made small iron facility was also investigated. One of the two vapor-depositable and glass-like monomers, the bifunctional 1,3-dibenzoic-5-tert-butylcoumarinester, showed crystals in larger areas of the resist film when heated under high vacuum. Unexposed monomers of the other material, monofunctional 3,5-di-tert-butylbenzoiccoumarinester, could be removed by thermal treatment under high vacuum, though (optimized conditions: 80 °C for 15 h). By doing so, an all-dry photolithography with a low molecular weight coumarin ester could be established. It was shown that a dimerization is sufficient to create an ample difference in melting points for a dry development. However, a dependency on the film thickness was noticed. Structures thicker than 30 nm seemed to melt while structures below 30 nm showed clear lines. A dependency of the glass-transition temperature in respect of the film thicknesses might be the reason for this observation.

In summary, this thesis proved the concept of PVD for the solvent-free preparation of low molecular weight, glassy photoresist films. Additionally, patterns were obtained and parameters such like composition and exposure dose could be efficiently optimized by the employment of combinatorial methods. The exposed films of the CARs were either developed with an optimized basic aqueous solution or, in two cases, even with pure water. The application of a newly synthesized coumarin derivative as a negative tone, low molecular weight photoresist allowed an all-dry photolithography, and was realized for the first time.

6. ZUSAMMENFASSUNG

Die vorliegende Arbeit beschäftigt sich mit der lösungsmittelfreien Herstellung von niedermolekularen, amorphen, lichtempfindlichen Fotolackfilmen, auch Fotoresistfilme genannt, mittels Aufdampfen im Hochvakuum (physikalische Gasphasenabscheidung, physical vapor deposition, PVD), ihrer anschließenden UV-Belichtung mit vorgeschalteter Maske und ihrer Entwicklung, um Strukturen im Mikro- und Nanometerbereich herzustellen.

Die genannten Prozesse sind elementare Schritte der so genannten Fotolithografie. Durch die Verwendung einer Maske werden nur bestimmte Teile des Films belichtet. In diesen Bereichen ändern sich aufgrund durch die Belichtung ausgelöster chemischer Reaktionen physikalische Eigenschaften wie zum Beispiel die Löslichkeit in bestimmten Lösungsmitteln. Im abschließenden Schritt der Fotolithografie, der Entwicklung, wird der generierte Unterschied ausgenutzt, um entweder *Positivstrukturen* (die belichteten Bereiche werden entfernt) oder *Negativstrukturen* (die unbelichteten Bereiche werden entfernt) herzustellen.

Die in unserer Gruppe entwickelten kombinatorischen PVD-Techniken gestatten sowohl die Erstellung von Gradienten oder Sektoren auf demselben Substrat als auch das gleichzeitige Aufdampfen mehrerer Substanzen (Coverdampfen), welche die Verwirklichung einer komplett trockenen Fotolithografie erleichtern. Durch den Einsatz von drei Effusionsquellen und fünf Sensoren, die individuelle Aufdampfraten und Schichtdicken messen, können organische Substanzen in einem genauen Verhältnis zueinander und mit einer definierten Schichtdicke aufgedampft werden. Während des Aufdampfens besteht die Möglichkeit, mit Hilfe von vorgeschalteten Masken in einem Maskenrondell nur ganz spezifische Sektoren auf dem Substrat zu bedampfen. Mittels exakter Positionierung des Maskenrondells und Veränderung der Quellentemperatur – und damit der Aufdampfraten – ist es möglich, eine so genannte Sektorenbibliothek kombinatorisch zu erstellen, um auf einem Substrat und während ein- und desselben Aufdampfprozesses Sektoren mit unterschiedlichen Zusammensetzungen mehrerer Komponenten zu erhalten.

In dieser Arbeit wurden zwei Arten von niedermolekularen, negativen Fotoresistystemen behandelt:

(1) Fotoresistsysteme, welche *molekulare Gläser* bilden und aus mehreren Komponenten bestehen, waren Bestandteil der Untersuchungen. Aus einer dieser Komponenten, einer Fotosäure (photoacid generator, PAG), wird durch Bestrahlung bei geeigneter Wellenlänge in mehreren Schritten eine Säure frei, welche bei kurzer Erwärmung des Systems (post-exposure bake, PEB) *katalytisch* eine Reaktion zwischen den anderen Komponenten auslöst. Dieser Prozess wird als chemische Verstärkung (chemical amplification) bezeichnet, da durch *ein* Photon eine Vielzahl von Reaktionen initiiert wird.

(2) Neuartige, mit sich selbst reagierende Cumarinderivate wurden synthetisiert und hinsichtlich ihrer Eignung für einen komplett trockenen Fotolithografieprozess untersucht. Zusätzlich wurde die Reduzierung der Belichtungszeit durch einen aufdampfbaren Sensibilisator erreicht.

(1) Physikalische Gasphasenabscheidung von niedermolekularen, glasartigen Fotoresists als neuartiger Zugang zur Strukturbildung durch chemische Verstärkung: Es wurden Untersuchungen und Charakterisierungen (DSC, TGA, HPLC) mehrerer niedermolekularer chemisch verstärkter Resists (chemically amplified resists, CARs) sowohl hinsichtlich ihrer Eignung für PVD als auch für anschließende Fotolithografieprozesse durchgeführt. Drei ternäre Systeme (**i**, **ii**, and **iii**) erwiesen sich als geeignet und erfüllten die Anforderungen (Aufdampfbarkeit, Bildung von glasartigen Filmen, fotostrukturierbar). Sie bestehen generell aus einem mehrwertigem Phenol, einem säureempfindlichen Vernetzer (*N*,*N*,*N*,*N*-Tetra(methoxymethyl)glycoluril, „Powderlink®“) und einem PAG:

i. 1,1,1-Tris(4-hydroxyphenyl)-1-ethyl-4-isopropylbenzen, Powderlink® und der nichtionische PAG 2-(4-Methoxystyryl)-4,6-bis(trichlormethyl)-1,3,5-triazin („Triazin“)

ii. 5,5’,6,6’-Tetrahydroxy-3,3,3’,3’-tetramethyl-1,1’-spirobisindan („Spirobisindan“), Powderlink® und der nichtionische PAG *N*-Hydroxynaphthalimidtriflat (“Triflat”)

iii. 6,6’,7,7’-Tetrahydroxy-4,4,4’,4’-tetramethyl-2,2’-spirobichroman („Spirobichroman“), Powderlink® und der nichtionische PAG *N*-Hydroxynaphthalimidtriflat (“Triflat”)

Mittels der kombinatorischen Maskentechnik der am Lehrstuhl eingesetzten PVD-Anlage wurden Sektorenbibliotheken erzeugt, um die Zusammensetzung der einzelnen CARs zu optimieren. Die Belichtungsdosis wurde kombinatorisch optimiert, indem jeder der Sektoren mit unterschiedlichen Dosen bei 365 nm belichtet wurde. Des Weiteren wurde die Entwicklung optimiert, indem unterschiedliche Verdünnungen der wässrigen Entwicklerlösung Tetramethylammoniumhydroxid (TMAH) mit diversen Eintauchzeiten eingesetzt wurden. Interessanterweise sind die Resists **ii** und **iii** durch reines Wasser entwickelbar, was einen Schritt in Richtung umweltfreundlichere Prozesse bedeutet. Mit der eingesetzten Technik konnten Strukturen von etwa 700 nm (**i**) beziehungsweise 400 nm (**ii** und **iii**) hergestellt werden. Die erzeugten Muster wurden mittels optischer Mikroskopie und Rasterelektronenmikroskopie betrachtet und die Qualität der Strukturen sowie die erreichte Auflösung verglichen, um die optimierten Zusammensetzungen und Belichtungsdosen der drei CARs zu ermitteln. Mittels HPLC-Analytik, die sich für die Problematik der Detektion geringer aufgedampfter Substanzmengen als sehr gut geeignet herausstellte, wurde die thermische Stabilität der eingesetzten Materialien sowie die Zusammensetzung in den einzelnen Sektoren bestimmt.

(2) Synthese von niedermolekularen Cumarinderivaten und eine auf ihnen basierende komplett trockene Lithografie: Der zweite Fotoresisttyp, der Gegenstand dieser Arbeit war, basiert auf mit sich selbst reagierenden Cumarinderivaten. Viele dieser Derivate unterliegen bei UV-Belichtung über 300 nm einer [2+2]-Cycloaddition. Dadurch können, je nach Anzahl der funktionellen Gruppen im Molekül, Dimere über Ketten bis hin zu Netzwerken entstehen. Die in dieser Arbeit vorgestellten zehn Cumarinester wurden bis auf ein Molekül zum ersten Mal synthetisiert und charakterisiert (NMR-Spektroskopie, HRMS, EA, DSC, TGA). Es wurden gezielt solche Derivate hergestellt, von denen man sich thermische Stabilität und amorphe Zustände versprach, um glasbildende Fotolackfilme mittels PVD herstellen zu können. Dabei wurden mehrere Substanzen gefunden, die ohne Zersetzung aufdampfbar waren. Zwei davon, 1,3-Dibenzyl-5-tert-butylcumarinester und 3,5-Di-tert-butylbenzylcumarinester, bildeten transparente, amorphe Filme, wie sie für die Strukturierung durch Fotolithografie notwendig sind. Da sich der durch die Belichtung gebildete Cyclobutanring bei einer Wellenlänge unterhalb 300 nm teilweise öffnet und sich die Monomere zurückbilden, wurde nur oberhalb dieser kritischen Wellenlänge gearbeitet. Dies führte allerdings aufgrund der geringen Überlappung mit dem Absorptionsspektrum des Cumarinderivats 3,5-Di-tert-butylbenzylcumarinester zu langen Belichtungszeiten

(50 Minuten). Mit Michlers Ethylketon wurde erfolgreich ein aufdampfbarer Sensibilisator gefunden, der die nötige Belichtungszeit für 3,5-Di-tert-butylbenzylcumarinester von 50 auf 5 min deutlich reduzierte, was mittels UV-Spektroskopie verfolgt werden konnte.

Da sich die oben genannten Cumarinderivatmonomere im Hochvakuum verdampfen lassen, wurde des Weiteren untersucht, ob nach der Belichtung die Monomere in den unbelichteten Bereichen in einer beheizbaren, eigens dafür gebauten Hochvakuumeinrichtung abgedampft werden können, um auf diese Weise eine völlig lösungsmittelfreie Fotolithografie auf Basis von Cumarinderivaten aufzubauen.
Eines der beiden aufdampfbaren und glasartigen Monomere, der bifunktionelle 1,3-Dibenzyl-5-tert-butylcumarinester, zeigte bei den Entwicklungsbedingungen in der Apparatur eine erhöhte Kristallisationsneigung in größeren Flächen, während das andere, der monofunktionelle 3,5-Di-tert-butylbenzylcumarinester, komplett entfernt werden und so eine trockene Fotolithografie mit einem niedermolekularen Cumarinderivat (optimierte Bedingungen: 80 °C, 15 Stunden Entwicklungszeit) durchgeführt werden konnte. Dadurch wurde gezeigt, dass eine Dimerisierung ausreicht, um den nötigen Schmelzpunktunterschied zu erhalten. Allerdings zeigte sich eine starke Schichtdickenabhängigkeit – die Strukturen schienen oberhalb einer Filmdicke über 30 nm zumindest teilweise zu verschmelzen, was mit einer Abhängigkeit der Glasübergangstemperatur von der Schichtdicke zusammenhängen könnte.

Mit dieser Arbeit konnte erfolgreich gezeigt werden, dass sich Filme von unterschiedlichen, niedermolekularen Fotoresistsystemen lösungsmittelfrei durch PVD herstellen lassen. Durch Fotolithografieprozesse ließen sich Strukturen erzeugen, und mittels Anwendung kombinatorischer Verfahren wurden unterschiedliche Parameter wie Zusammensetzung und Belichtungsdosis effizient optimiert. Die belichteten Filme der CAR-Fotolacke wurden durch eine optimiert verdünnte wässrig-basische Lösung beziehungsweise in zwei Fällen sogar durch reines Wasser entwickelt.
Mittels eines neu synthetisierten Cumarinderivats konnte ein niedermolekularer Negativresist entwickelt und eine vollständig trockene Fotolithografie umgesetzt werden, was auf Basis dieser Substanzklasse zum ersten Mal durchgeführt wurde.

7. INDIVIDUAL CONTRIBUTION TO JOINT PUBLICATIONS

I wrote the first drafts of all manuscripts which where finalized jointly with Dr. Christian Neuber and Prof. Dr. Hans-Werner Schmidt. The asterisk denotes the corresponding author.

A1

Physical Vapor Deposition of Molecular Glass Photoresists: A New Route to Chemically Amplified Patterning

Frauke Pfeiffer, Nelson M. Felix, Christian Neuber, Christopher K. Ober,* and Hans-Werner Schmidt*

Advanced Functional Materials **2007**, *17*, 2336-2342

I established the preparation and composition optimization of low molecular photoresists by physical vapor deposition (PVD). Amongst others, a vapor depositable, non-ionic photo acid generator was found. Furthermore, with support of Martha Gietl, technical assistant in our group, I developed an HPLC method for quantitative and qualitative measurements of single and coevaporated material. Finally, while staying at Cornell University, I optimized development conditions and characterized the resulting patterns by optical microscopy. The exposure of the prepared photoresist films as well as some optical microscopy and SEM characterization was performed by Nelson Felix, Cornell University. Further SEM measurements were performed by Clarissa Abetz. Sven Adolph from EPFL performed one measurement with UPLC/MS (MS^2).

A2

Towards Environmentally Friendly, Dry Deposited, Water Developable Molecular Glass Photoresists

Frauke Pfeiffer, Nelson M. Felix, Christian Neuber, Christopher K. Ober,* and Hans-Werner Schmidt*

Advanced Materials ***2007****, intended for submission* (this manuscript has been accepted meanwhile and is published: *Phys. Chem. Chem. Phys.*, ***2008***, *10*, 1257-1262)

The complete sample preparation including varying compositions by PVD was performed by me. Additionally, HPLC characterization of the evaporated compounds, overcoming the issue of autoxidation of spiro compounds, was developed by me with support of Martha Gietl. Nelson Felix of Cornell University exposed, developed and characterized the obtained patterns by optical microscopy.

A3

Synthesis and All-Dry Lithography of Glass-Like Coumarin Derivatives

Frauke Pfeiffer, Christian Neuber, and Hans-Werner Schmidt*

Chemistry of Materials ***2007****, intended for submission*

I synthesized and characterized (NMR, TGA, DSC, UV-Vis) all substances with the exception of three, which where synthesized under my supervision of student Frank Lüdel. All samples were prepared by PVD, exposed, developed and characterized (optical microscopy) by me or within my charge. The vacuum development equipment was devised jointly with Dr. Christian Neuber and built by the mechanic's workshop of Universität Bayreuth.

A4

All-Dry Processing of a Negative Tone Photoresist based on a Low Molecular Weight Coumarin Derivative

Frauke Pfeiffer, Christian Neuber, and Hans-Werner Schmidt*

Advanced Materials ***2007****, intended for submission*

The investigated substance was synthesized and characterized (NMR, TGA, DSC) by me. I prepared the photoresist films by PVD and performed the optimization of exposure dose, development time and temperature. I characterized the resulting structures by optical microscopy. Additionally, I investigated and applied a vapor-depositable sensitizer which reduced the exposure time significantly.

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Physical Vapor Deposition of Molecular Glass Photoresists:
A New Route to Chemically Amplified Patterning**

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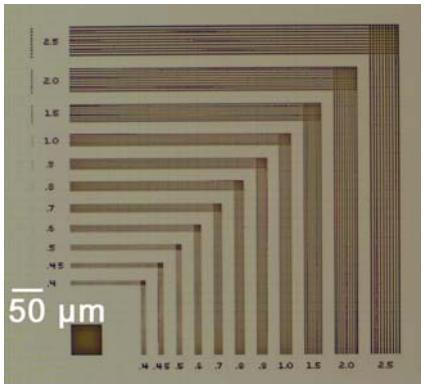
Graphical Abstract



A negative tone photoresist based on a molecular glass was prepared by physical vapor deposition. A combinatorial approach was utilized to aid optimization of the photoresist by systematic variations in compositions, exposure doses, and development conditions and thus the pattern formation.

Abstract

A negative tone photoresist film, consisting of a molecular glass, a photoacid generator, and an acid labile crosslinker, was prepared by physical vapor deposition, a solvent-free process. Subsequent to deposition, the coevaporated monomers were exposed using 365 nm radiation, subjected to a post exposure bake step, and developed in aqueous base to produce sub-micron patterns. Combinatorial techniques were used to aid optimization of the photoresist by systematic variations in composition and exposure dose. Development factors such as concentration and time were also optimized.

1. Introduction

The ability to create small structures has for decades been a hallmark of the semiconductor industry. Fabrication of sub-micron structures is now possible due to continuous advances in the technology of photoresists, which are the materials that are patterned and developed to form the target features in any photoresist pattern.[1] As feature sizes shrink, photoresists ("resists") must constantly evolve to adapt to changing wavelengths of imaging radiation. Since photoresists are usually based on polymers, their molecular size is rapidly becoming one of their limiting factors. In the last decade it has been shown that small molecules with glassy properties, so called molecular glasses, can serve as resist materials as well,[2-6] and recently, thermally stable star-shaped molecules with high glass transition temperatures have been introduced.[7,8]

Usually, the necessary resist films needed for high resolution imaging are deposited by casting from solution via spin coating or doctor blading techniques, depending on application. One of the disadvantages of these solution-based methods is that solvents may contain dust or other high boiling residues, which causes a rougher surface or leaves impurities in the film. Another problem is that solvent-based processing is wasteful in terms of solvent use and loss

of valuable resist materials. Direct deposition of photoresist materials therefore has the potential to improve deposition performance and for reducing process waste.

Compared to casting films from solution, there are several additional advantages of using physical vapor deposition (PVD) for photoresists. The resulting films are very uniform and can be produced with a precise thickness in the nanometer range, even on surfaces that have a wide range of curvature. Substances that are not soluble enough for casting purposes may form films. However, such materials require thermal stability and a suitable molecular weight for vapor deposition. A further advantage for the efficient screening of photoresist compositions is the applicability of a combinatorial PVD approach.[9] This approach was successfully utilized in the optimization of thin film multilayer devices such as organic light emitting diodes (OLED)[10-12] and vapor deposited organic solar cells.[13,14] The combinatorial approach allows the investigation of libraries of different material combinations and device configurations and is the most efficient way to screen materials and optimize devices under identical conditions even with internal references, all in one experiment.

The paper addresses the approach towards sub-micron lithography by using PVD to process the photoresist film composed of a low molecular weight molecular glass, a crosslinker, and a photoacid generator (PAG). After irradiation and a post exposure bake (PEB) step the development results in a negative tone photoresist (Fig. 1).

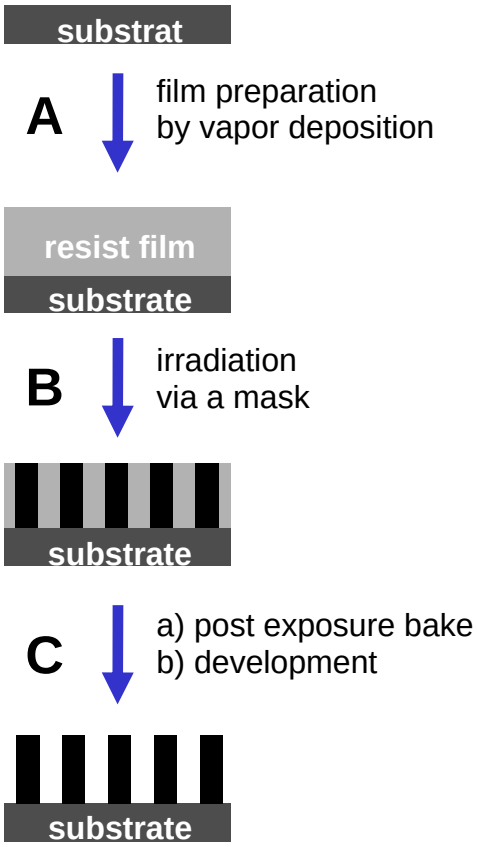


Figure 1. Schematic representation of the process of forming a negative tone image via physical vapor deposition (PVD) of the photoresist film.

A) The photoresist film is prepared by coevaporation of molecular glass, crosslinker, and photoacid generator (PAG).

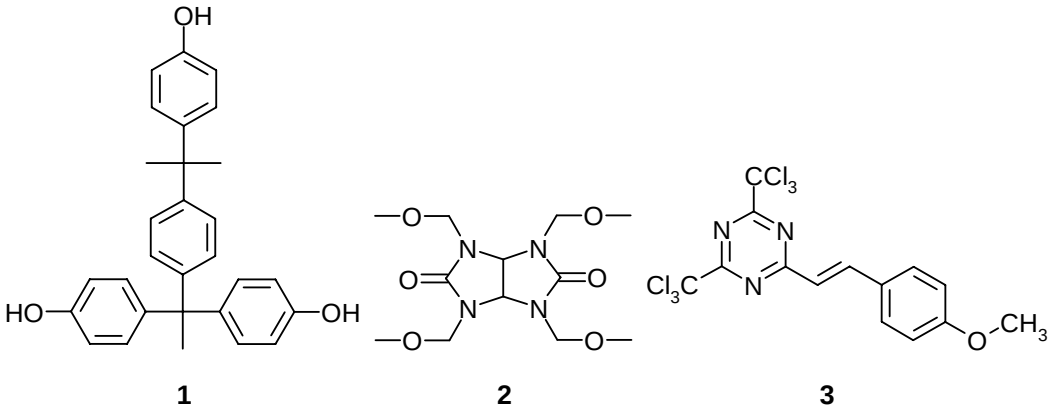
B) During irradiation via a mask a strong acid is generated in the exposed areas of the film.

C) a) During the post exposure bake (PEB) step, chain extension and crosslink reactions occur.

b) The unexposed areas are soluble in the developer. This results in a negative tone photoresist.

The following materials were used in our studies of PVD processed molecular glass photoresists (Scheme 1). A glassforming trisphenol, 1,1,1-tris(4-hydroxyphenyl)-1-ethyl-4-isopropylbenzene ("trisphenol") **1** was used as major component of the photoresists. This trisphenol and similar derivatives have been used as starting materials for polymers, e.g. novolak resins[15] or as curing agent for epoxy resins.[16] In addition, a tetra-functional substance *N*,*N*,*N*,*N*-tetra(methoxymethyl)glycoluril ("Powderlink®") **2** was used as acid labile crosslinker. Powderlink® is most commonly known as an agent in coatings and lacquers,[17] often in combination with polyesters.[18,19] In lithography it has been used as the crosslinking reagent for etch resistant antireflective coatings as an undercoated layer for resists[20,21] and also in negative photoresist formulations containing fluoropolymers.[22] The application of Powderlink® in a low molecular weight resist as performed here is a new way to use this crosslinking agent and has only been used once before in a molecular glass resist.[23] The third

component is a nonionic photoacid generator (PAG) which has to be stable enough to be deployed in the physical vapor deposition process. This means that it must have sufficient chemical stability and volatility to be used in the process. In this study we investigated 2-(4-methoxystyryl)-4,6-bis-(trichloromethyl)-1,3,5-triazine ("triazine") **3**. The function of a PAG is to provide protons when exposed to certain wavelength radiation. For the triazine PAG, UV radiation below 400 nm produces hydrochloric acid, which catalyzes the crosslinking reaction between trisphenol and Powderlink®. Contrary to polymeric resist systems, these small molecule resist components were found to be suitable for the PVD process.



1 **2** **3**

Scheme 1. Chemical structure of the three components in the investigated photoresist system. 1,1,1-tris(4-hydroxyphenyl)-1-ethyl-4-isopropylbenzene ("trisphenol") **1**, acid labile crosslinker *N,N,N,N*-tetra(methoxymethyl)glycoluril (Powderlink®) **2** and photoacid generator (PAG) 2-(4-methoxystyryl)-4,6-bis-(trichloromethyl)-1,3,5-triazine ("triazine") **3**.

In the following we demonstrate the feasibility of physical vapor deposition of molecular glass photoresists and the combinatorial approach to efficient optimization of compositions and exposure doses.

2. Results and Discussion

2.1 Combinatorial vapor deposition

The described combinatorial technique is used for the first time to optimize the composition of a photoresist. The core piece of the combinatorial vapor deposition is a rotating system consisting of a positionable mask holder with five different, exchangeable masks in combination with a positionable substrate holder and a shutter. Each mask can be positioned in front of the substrate to allow the vapors to deposit through the specific opening of the mask, producing different sectors on the substrate. A schematic representation of the PVD

chamber, including the sources and the masks setup, with the possibility to coevaporate up to three substances is shown in Figures 2a and 2b.

For combinatorial experiments, one of the masks was put into position. The sources were heated individually to obtain a certain evaporation rate ratio monitored by the quartz crystal sensors at each source. When the desired ratio was reached, all shutters at the sources and at the substrate were simultaneously opened, and the vapor deposited onto the designated sector. During evaporation, the combinatorial setup itself was rotating to receive a uniform film. After having reached a preset film thickness which was measured by the sensors nearby the substrate, the shutters were closed and the second mask was positioned below the substrate. By changing the temperature of the sources, the evaporation rates were set to the next coevaporation ratio. This procedure was repeated for each sector. In the described combinatorial experiments, five sectors with different compositions were prepared on one half of the substrate (Fig. 2b). Rotating the substrate holder 180^{o} allowed the preparation of five additional sectors.

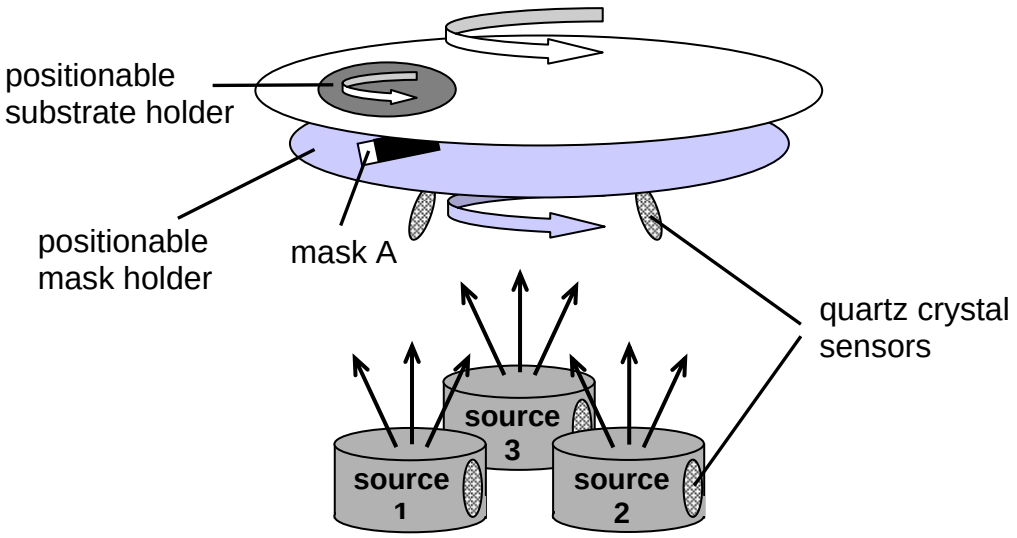


Figure 2a. Schematic representation of coevaporation by PVD using a setup to prepare combinatorial composition libraries. Within the vacuum chamber, the arrangement contains a positionable mask holder with up to five different, exchangeable masks which can be positioned by rotation below the substrate. The complete setup rotates during evaporation to obtain a uniform film. Each source has its own precise heating to individually control the evaporation rate. The evaporation rate is measured by a total of five quartz crystal sensors. By these means sectors with defined compositions can be prepared and combinatorial libraries are created.

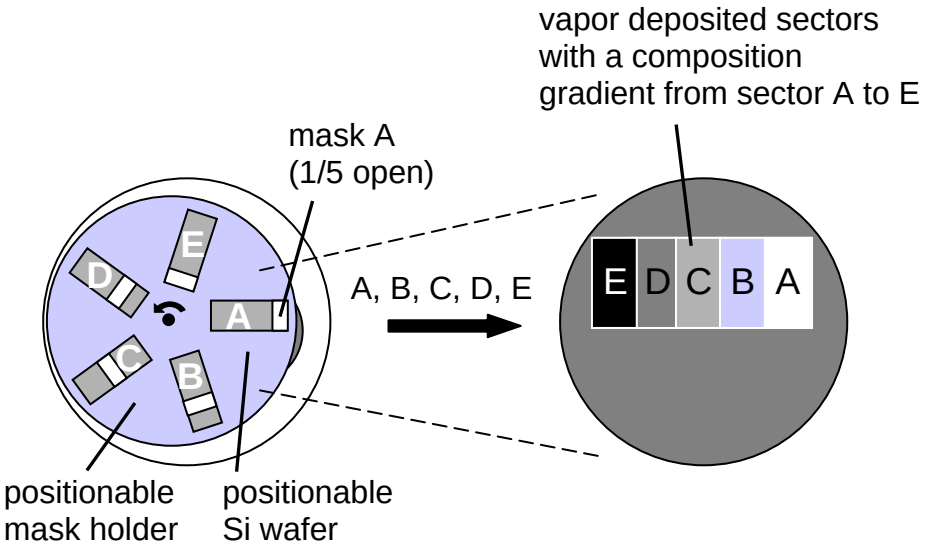


Figure 2b. Schematic representation of the combinatorial preparation of five sectors with different compositions (view from bottom). After a predetermined film thickness of sector A is reached, the evaporation rates are adjusted to obtain a different ratio, and mask B is positioned. Then sector B is fabricated by PVD. After five sectors are produced, the substrate can be rotated 180^{o} and additional five sectors of different compositions can be prepared.

2.2 Vapor deposition of photoresist components

For our investigation we used the previously described glasslike negative tone photoresist system consisting of the following monomers: trisphenol **1** is the major component, acid labile Powderlink® 1174 **2** serves as crosslinker and triazine **3** is a light-sensitive photoacid generator (PAG). Photoresist films of about 100 nm thickness and consisting of above mentioned materials were prepared by physical vapor deposition (PVD). One of the critical points in our studies was to establish the effect of PVD on the photoresist composition and function. High pressure liquid chromatography (HPLC) analysis was found to be highly applicable for this purpose. For this, we had to inspect the UV spectra of the substances for identifying suitable wavelengths for the UV detector of the HPLC. Triazine has a smaller maximum at 248 nm and a larger one at 373 nm. Trisphenol shows a big maximum at 208 nm and a smaller one at 273 nm. The UV absorption of Powderlink® starts significantly at 220 nm and increases towards smaller wavelengths until the measurement stops at 200 nm. Hence, 373 nm for triazine, 273 nm for trisphenol, and 201 nm for Powderlink® were used for HPLC detection. Under the in the experimental part described conditions, triazine has a retention time of about 6.72 minutes, trisphenol of about 3.94 minutes and Powderlink® of about 1.65 minutes. Inspecting the HPLC data (Fig. 3) of the substances after single PVD and comparing it to that of the non-evaporated substances, it was shown that triazine is vapor depositable without any issues. Trisphenol showed a second, smaller peak. When evaporating

fresh material, the area of this second peak was very small, about 1 % of the area of the trisphenol peak. It was found that when using source material that had already melted several times from prior evaporation processes, the area of the second peak increased with the number of reusage of the melted substance to equal a third of the total area. This indicates that trisphenol partly decomposes. UPLC-MS analysis proved the first peak to be trisphenol. The second peak has a mass of M^- of 329. The difference of 94 suggested that a phenol group was cleaved to give a bisphenol with a double bond. This was shown by MS^2 and NMR. Powderlink® seemed to readily desorb from the substrate when evaporated alone since no substance could be found on the wafer. However, after coevaporation with trisphenol, the characteristic peaks were easily observed by HPLC. This shows that a single PVD step with Powderlink® is not possible under normal circumstances. The reason for this observed behavior might be that the molecular weight of Powderlink® is too small to prevent desorption. But when coevaporated, Powderlink probably forms hydrogen bonds with trisphenol which decreases the likelihood of desorption.

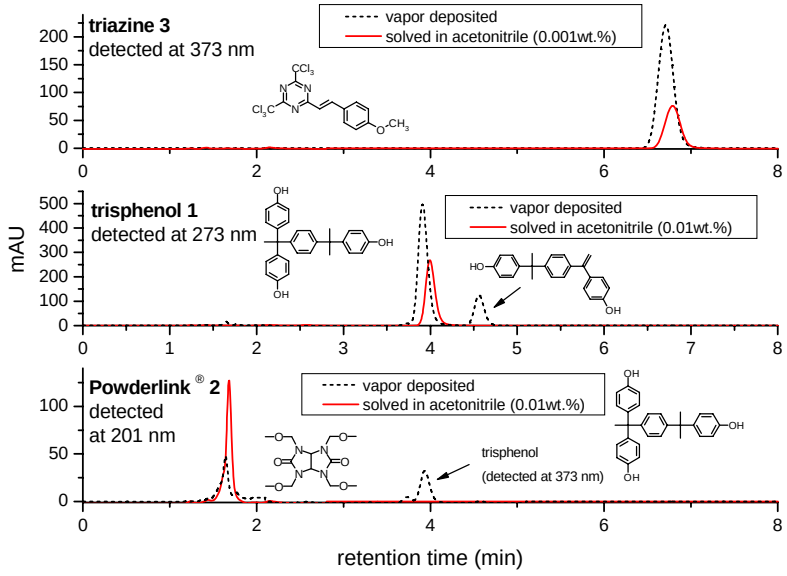


Figure 3. HPLC measurements of triazine **3**, trisphenol **1**, and Powderlink® **2**, showing the traces before (solid lines) and after PVD (dashed lines). The slight shift of peaks belonging to the same substance is due to different amounts of sulfuric acid in the mobile phase (80vol% acetonitrile, 20vol% deionized water).

Triazine and Powderlink® are completely thermally stable. Trisphenol is thermally stable as long as fresh material is used. It is partly cleaved, though, when using the same melted material repeatedly from previous evaporation processes. The first peak was proven to be trisphenol, while the second one is a bisphenol with a double bond, as identified by NMR and mass spectrometry. The trisphenol peak in the trace of the Powderlink® assay is due to the fact that Powderlink® desorbs from the substrate when evaporated alone so there must be coevaporation carried out for that substance. The detecting UV wavelengths were 373 nm for triazine, 273 nm for trisphenol and 201 for Powderlink®.

A calibration with the non-evaporated substances, dissolved in acetonitrile, has been carried out by HPLC to verify the composition in wt.% in the prepared sectors derived from the measured evaporation rates during coevaporation.

2.3 Photoresist Optimization

To determine the optimized composition of this negative resist a combinatorial approach to generate a library was used. Ten different sectors each with a systematic variation of the three components on the same silicon wafer (Table 1) were created. This was achieved by coevaporating trisphenol, Powderlink® and triazine at the same time and adjusting the composition ratio by measuring the evaporation rates. By increasing the evaporation rate of trisphenol from 67wt.% to 96wt.% (sectors A to E) and of triazine from 0.4wt.% to 6.6wt.% (sectors F to J) respectively, the ratios for the various sectors differed broadly. Using different masks in front of the substrate allowed the vapor to deposit only on the desired areas of the substrate.

Table 1. Combinatorial library for optimizing the composition of the photoresist. Different compositions of Powderlink®, trisphenol and PAG triazine in the ten sectors (A to J) on the silicon wafer were prepared. The ratios were calculated by an HPLC calibration which provided a correlation between evaporation rates and composition. From sector A to E, the evaporation rate—and thus the wt.%—of trisphenol, and from sector F to J the evaporation rate of triazine was increased.

sector	Powderlink® on wafer [wt.%]	Trisphenol on wafer [wt.%]	PAG on wafer [wt.%]
A	32.6	67.3	0.1
B	24.4	73.8	1.8
C	12.6	86.7	0.7
D	7.2	92.7	0.1
E	3.9	96.0	0.1
F	14.9	84.7	0.4
G	14.9	84.4	0.7
H	15.1	83.3	1.6
I	14.0	82.0	4.0
J	12.8	80.6	6.6

Each sector was then exposed in defined regions to doses of 40, 240, 440, 640, 840 or 1040 mJ cm^{-2} of UV light (Fig. 4) at 365 nm so that with one wafer the composition as well as the dose could be quickly optimized by this combinatorial approach.

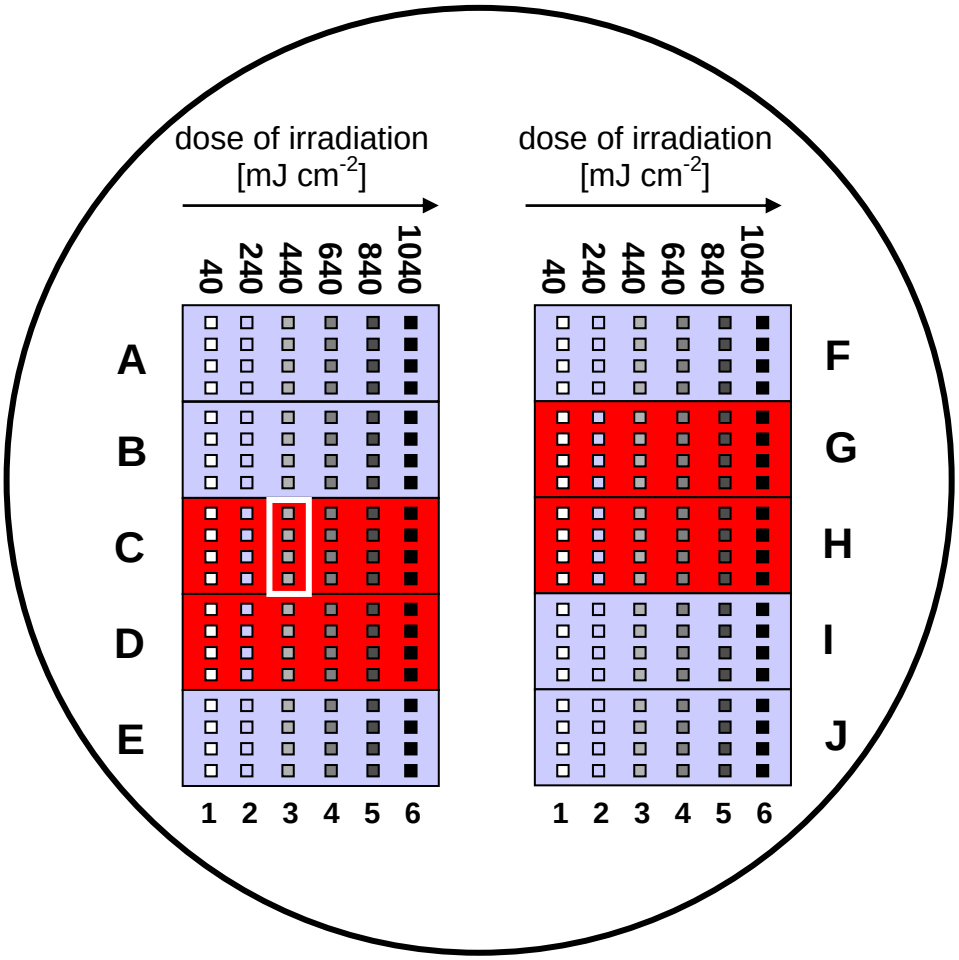


Figure 4. Schematic representation of the library fabricated by a combinatorial approach of coevaporating **1**, **2**, and **3** to optimize the composition and the dose of irradiation. In each of the ten sectors with different compositions, the dose of irradiation at 365 nm increased from left to right (from 40 mJ cm^{-2} to 1040 mJ cm^{-2}). Four sections showed good patterns after development (highlighted). The optimized composition, 12.6wt.% Powderlink®, 86.7wt.% trisphenol, 0.7wt.% PAG triazine, was found in sector C3, exposed to 440 mJ cm^{-2} (white framed).

A post exposure bake (PEB) was performed at 90 °C for 30 s. The dependence on the composition can be easily observed comparing sectors C3 and J3, shown in Figures 5a and 5b. While the best sector C3 (Fig. 5a;12.6wt.% Powderlink®, 86.7wt.% trisphenol and 0.7wt.% triazine) shows sharp lines and no residues after development, the increased amount of triazine in J3 (Fig. 5b;composition: 12.8wt.% Powderlink®, 80.6wt.% trisphenol, 6.6wt.%

triazine), caused crystals which could not be removed by the developer tetramethylammonium hydroxide (TMAH).

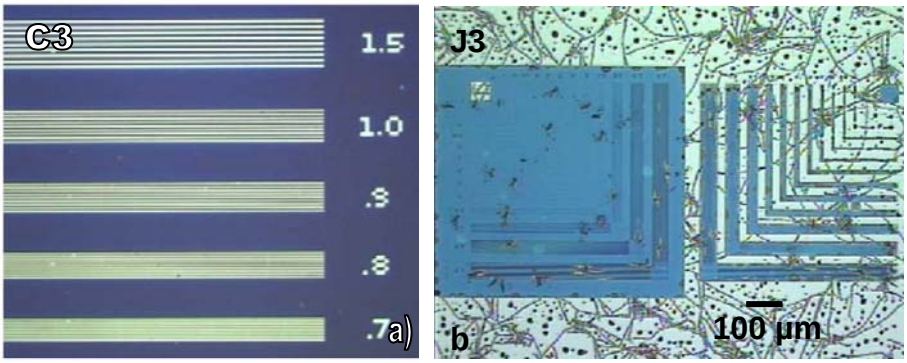


Figure 5. Reflection microscope images taken for the optimization of the composition.
a) The optimized sector C3 after PEB and development. The white lines are the exposed parts, the darker area is the surface of the silicon wafer. The numbers indicate the line width in microns. The optimized composition of 12.6wt.% Powderlink®, 86.7wt.% trisphenol and 0.7wt.% PAG triazine was exposed to a dose of 440 mJ cm^{-2} at 365 nm and baked at 90°C for 30 s. After patterning, the wafer was dipped into a diluted TMAH solution (1:27 (0.26 N TMAH:deionized water)) for 6 seconds, rinsed with deionized water afterwards. No residues can be observed.
b) The unoptimized sector J3, after PEB and development, with a different composition than C3 (exposure dose 440 mJ cm^{-2} at 365 nm). The darker parts are exposed. Composition: 12.8wt.% Powderlink®, 80.6wt.% trisphenol, 6.6wt.% triazine. Development in 1:27 TMAH solution (0.26 N TMAH:deionized water) for 6 s, rinsed with deionized water afterwards. Crystalline residues are observable.

Since 0.26 N TMAH, the standard TMAH concentration for lithography purposes, was found to be too concentrated, the development step was performed in a diluted TMAH solution (1:27 (0.26 N TMAH:deionized water)). The reason for this sensitivity might be the lower crosslinking rate because of the nonionic and thus less effective PAG, and the thinner layer thickness in the nanometer range than applied in commercial photoresists.

The wafer was dipped into the developer solution for a specified time, e.g. 6 seconds, then removed and thereafter carefully rinsed with deionized water and dried using compressed air.
Prior to film preparation by PVD, the investigated resist was prepared by spin coating from a 10wt.% solution of propylene glycol monomethyl ether acetate (PGMEA) to ensure the pattern formation . The prescreening experiments resulted in suitable composition ratios of 80wt.% trisphenol, 15wt.% Powderlink® and 5wt.% PAG. In this case an ionic PAG was utilized, whereas the non-ionic triazine PAG was used for the PVD experiments. The spin coated sample was exposed to a dose of 440 mJ cm-² at 365 nm, a PEB was performed and it was developed in diluted TMAH solution (1:20 (0.26 N TMAH:deionized water)). This was

done for preparing a reference pattern to examine the potential of the evaporated photoresist system with regard to pattern resolution and residual material after development.
The quality of the patterns observed by reflection microscope or SEM (not shown here) was used as a comparison reference for the optimization.
Though in theory, judging by the number of functional groups, the stoichiometric composition of Powderlink® and trisphenol is 1:1.6, the above described experiment showed the optimized ratio of Powderlink® and trisphenol to be about 1:7 at an exposure dose of 440 mJ cm^{-2} at 365 nm. A higher ratio of Powderlink® or instead a triazine concentration of more than 1wt.% resulted in crystals in the unexposed areas that could not be removed during the development step without destroying some portion of the patterns because of an overly long development time. Additionally, the resolution itself became worse with an increasing amount of Powderlink® judging by the observed patterns. The smaller lines (900 nm and smaller) were no longer separated.

In a second experiment, the development time and effect of concentration of the developer solution was investigated for a photoresist film prepared by PVD. This time, only one composition, the optimized composition from the first experiment (12.6wt.% Powderlink®, 86.7wt.% trisphenol, 0.7wt.% PAG triazine) and one exposure dose of 440 mJ cm^{-2} were used. After PEB at 90 °C for 30 s, the wafer was cut into smaller pieces and dipped into different concentrations of TMAH ranging from undiluted 0.26 N aqueous TMAH to 1:200 (0.26 N TMAH:deionized water) solution for different times (1 s to 600 s). The resulting patterns were observed by SEM and reflection microscopy. It was found that if the solution was higher concentrated than 1:10, the development was so fast that the patterns were stripped from the substrate within milliseconds. Judging from the resulting patterns, the optimal dilutions ranged between 1:20 and 1:50 (Fig. 6a). The lines were sharp, and no residues were observed. The development even worked with a dilution of 1:100, but resulted in residue in the unexposed areas and fringed light lines (Fig. 6b), indicating that the concentration of the developer is too low. The patterns were in the initial stages of being destroyed, but the unexposed areas were still not completely removed. A dilution of 1:200 gave no patterns regardless of the development time, and no substance is removed.

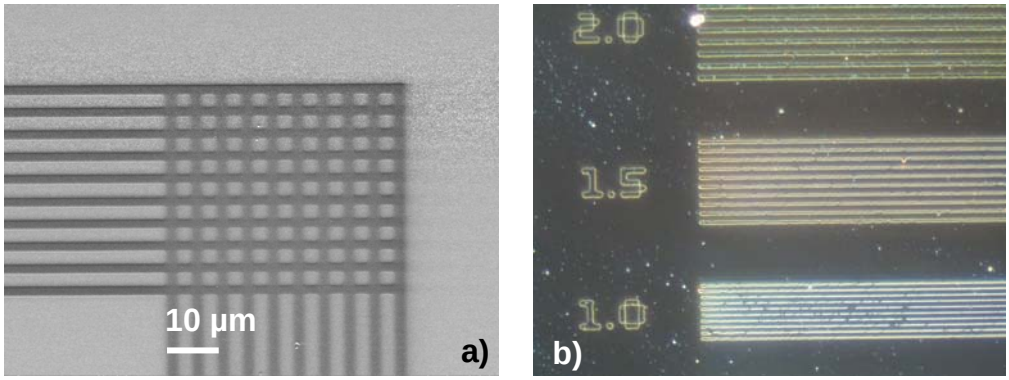


Figure 6. Images taken for the optimization of development conditions. One 4 inch wafer was completely prepared with an optimized composition (12.6wt.% Powderlink®, 86.7wt.% trisphenol, 0.7wt.% PAG) and patterned (440 mJ cm^{-2}).

a) Scanning electron microscope image (tilted 30° backwards) of a wafer section with optimized development conditions 1:40 TMAH solution (0.26 N TMAH:deionized water) for 13 s, rinsed with deionized water afterwards. The dark lines are the exposed regions. The lines are sharp, and no residue can be observed.

b) Reflection microscope image of an example of unoptimized development conditions: 78 s in 1:100 TMAH solution (0.26 N TMAH:deionized water), rinsed with deionized water afterwards. The numbers indicate the line width in microns, the light areas are the exposed sections. The lines are fringed, and there is still some residue in the unexposed areas. This result shows that the developer was too diluted.

3. Conclusions

Molecular glass photoresist films were deposited by physical vapor deposition. By this, producing negative tone photoresist films was achieved in a solvent-free manner. The monomers were coevaporated with controlled composition ratios on an unprimed silicon wafer, exposed, baked and developed. High pressure liquid chromatography was used to verify the thermal stability of the compounds and, after calibration, to derive the actual composition of the photoresist sections on the silicon wafer. Combinatorial techniques, i.e. producing a composition library on one wafer, aided the optimization of monomer composition and the required exposure dose. The development was improved by using PVD to produce a film with an optimized composition on an unprimed silicon wafer, then breaking the substrate into smaller pieces to obtain different test wafers with the same composition for systematically varying the developer dilutions and development times. In this manner, sub-micron negative tone patterns were successfully produced. In general, molecular glasses applied in films enable decreasing line widths because of their smaller size compared to polymer dimensions. But the limiting factor of chemically amplified resist systems is also the diffusion of the formed acid. Experiments regarding this issue were not performed in this work. For a further improvement of this photoresist system and to achieve smaller linewidth

in the nanoscale range, the PAG has to be optimized in terms of higher sensitivity and reduced diffusion. Alternatively, the use of molecular glasses consisting of self-reacting molecules without a PAG might overcome this issue, too.

4. Experimental

Materials: 1,1,1-tris(4-hydroxyphenyl)-1-ethyl-4-isopropylbenzene, **1**, 98 % was purchased from ABCR. Powderlink® 1174 (N,N,N,N-tetra(methoxymethyl)glycoluril), **2**, was provided by Worlée-Chemie GmbH and 2-(4-Methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine, **3**, 98 % was purchased from Aldrich. The developing solution, tetramethylammonium hydroxide (TMAH), was purchased from Aldrich as a 10wt.% solution in water. Propylene glycol methyl ether acetate (PGMEA) from Merck was used as a solvent for spin coating. All chemicals were employed without any further purification.

Characterization: High pressure liquid chromatography (HPLC; Agilent 1100 Series) characterization allowed conclusions on the chemical stability of the substances, the correlation of the measured film thickness/evaporation rates of the quartz sensors to the amount of deposited material, and most importantly, directly the determination of the composition of the three materials on the wafer.

The general thermal stability of the vapor deposited substances was tested by NMR, spectra taken before and after sublimation. NMR measurements were performed with Bruker 250 MHz in deuterated DMSO. To further check the thermal stability and a potential byproduct formation, HPLC analysis with a ZORBAX Bonus-RP C14 column was used. Suitable wavelengths for being able to detect independably the different substances with HPLC were determined by UV spectra (Spectrophotometer Hitachi U-3000). The following wavelengths were used for HPLC detection: 373 nm for triazine, 273 nm for trisphenol, and 201 nm for Powderlink®. After that, a test run with each of the substances dissolved in acetonitrile solution (triazine: 0.001wt.%, trisphenol and Powderlink®: 0.01wt.%) was performed to determine suitable conditions and the characteristic retention times of the substances. The injection volume for every sample was 25 µl, the mobile phase consisted of 80vol% acetonitrile and 20vol% deionized water (containing five drops of concentrated sulfuric acid per liter). The flow rate was 1 mL min^{-1}. To study the thermal stability of the substances, vapor deposition of the individual components on 15 mm × 15 mm silicon wafer pieces was performed. Afterwards the films were analyzed by HPLC, using 100 µl of acetonitrile to rinse the film off the wafer and additional 200 µl to dilute the sample solution.

The compositions of the deposited resist films were determined by establishing an HPLC calibration for each substance using the parameters as described above. This was used to verify the evaporation rates with the actual results obtained by HPLC measurements.
UPLC/MS (MS^2) spectra has been measured with Waters Acquity UPLC System with 2996 PDA detector and MicroMass Q-TOF micro with ES ion source.
Images were taken with reflection microscope Olympus MX50 and scanning electron microscope LEO 1530, operating at 5kV.
Film thicknesses were determined with a DekTak® 3 profilometer.
All production steps were performed under yellow light.

Film preparation by physical vapor deposition: For PVD, a Balzers PLS 500 with three heatable sources was used. Each source has its own shutter and sensor for adjusting the evaporation rates of each compound prior to the deposition. Each of the three quartz tubes was filled with about three hundred milligrams of triazine, Powderlink®, or trisphenol, and put in one of the sources. The films were prepared on polished N-type (100) 4 inch wafers, cleaned with acetone and isopropanol on a spin coater at 2000 rpm. The typical film thickness ranged between 90 and 120 nm. Triazine, Powderlink® and trisphenol were coevaporated at 7 × 10^{-6} mbar at different evaporation rates. The evaporation rate of triazine ranged from 2 to 23 Å s^{-1}, of trisphenol from 48 to 62 Å s^{-1}, and of Powderlink® from 15 to 40 Å s^{-1} which were measured with oscillating quartz crystals at the sources. Near the substrate two additional quartz crystals were installed to measure the final film thickness.

Film preparation by solution processing: For comparison, films were also prepared by spin coating. This was performed with a Siemens Coros OP15 at 2000 rpm for 30 s onto polished N-type (100) 4 inch silicon wafers which were precleaned with acetone and isopropanol. The resist composition was 5wt.% triazine, 15wt.% Powderlink® and 80wt.% trisphenol as 10wt.% solution in PGMEA. 200 nm thick films were produced. After spin coating, post applied bake (PAB) at 115 °C for 60 s was performed.

Exposure: The sectors were exposed with a GCA-6300 10X i-line Stepper (Zeiss lens with 0.42 N.A., 10 × 10 mm field size, resolution to 0.5 µm) through a mask (features from 2000 nm to 450 nm) with doses of 40, 240, 440, 640, 840 or 1040 mJ cm^{-2} at an exposure wavelength of 365 nm. Afterwards, a post exposure bake (PEB) at 90 °C for 30 seconds was performed.

Development: The development was performed by dipping wafer pieces for different lengths of time into various diluted aqueous tetramethylammonium hydroxide (TMAH) solutions (basic solution 0.26 N TMAH, dilutions ranged from 1:10 (0.26 N TMAH:deionized

water) to 1:100 (0.26 N TMAH:deionized water)). Afterwards, they were carefully rinsed with deionized water and dried using compressed air. The resulting patterns were compared by reflection microscope and scanning electron microscope (SEM).

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Towards Environmentally Friendly, Dry Deposited, Water Developable Molecular Glass Photoresists

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Abstract

Photoresists based on molecular glasses are gaining more and more importance as resist material to replace polymer based photoresist. In addition environmental issues have to be considered in the long-term. Therefore the paper describes novel negative photoresists containing a ternary mixture of a glassy low molecular functional polyphenol where the film preparation is possible by solvent-free physical vapor deposition. After UV light exposure and a thermal annealing process to enable acid catalyzed crosslinking between the molecular glass and the crosslinker, the photoresist was developed using only water to give well-defined

patterns. In order to experimentally study efficiently the multiple parameters such as composition, exposure dose, and development times combinatorial PVD techniques were utilized.

Introduction

Photoresists are necessary for the production of many different industrial and daily-use products such as computers, mobile phones, and consumer electronics. They are mainly used in the manufacture of integrated circuits like microchips,[1] but are also finding use in the developing fields such as biotechnology or photonics. However, in all the these new applications, complex surface topography, minimal solvent usage and mild development conditions are all advantages since patterning will increasingly take place on organic or other delicate substrates. One of the current challenges in high-resolution photolithography is the fact that photoresists are usually polymer-based. The very size of the polymer molecule, comparable to the target image size of many next generation lithographies, is one of the limiting factors in today's photoresists. Recently it was shown that small molecules which possess glassy properties, so called molecular glasses, can serve as photoresist materials as well.[2, 3] Molecular glasses have the advantage that their small molecular size enables high resolution patterning,[4] but they also have distinct and potentially superior solubility[5] and they can be vapor deposited[6] in contrast to polymeric resists. In this paper we would like to describe a new molecular glass photoresist process that translates these differences into new photoresists using solvent free dry deposition and water only development processes.

Experimental

Substances

6,6',7,7'-tetrahydroxy-4,4,4',4'-tetramethyl-2,2'-spirobichroman **1** 98% and 5,5',6,6'-tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-spirobisindane **2** 98% were purchased from ABCR. Powderlink® 1174 (N,N,N,N-tetra(methoxymethyl)glycoluril) **3** 100 % was provided by Worlée-Chemie GmbH. N-Hydroxynaphthalimide triflate **4** 98 % was purchased from Aldrich. Ascorbic acid 100% for HPLC analysis was bought at a local pharmacy. All substances were employed without any further purification.

Film preparation by combinatorial physical vapor deposition

For PVD, Balzers PLS 500 was used. Polished n-type (100) 4 inch unprimed silicon wafers served as substrates. They were precleaned with compressed air and thereafter cleaned with aceton and isopropanol on a spin coater (Siemens Coros OP15) at 2000 rpm. The substances were coevaporated at 7×10^{-6} mbar at different evaporation rates which were measured with oscillating quartz crystals at the sources in the vacuum chamber. Near the substrate two further quartz crystals are installed to quantify the film thickness. The PVD chamber contains a combinatorial setup to prepare sectors with different compositions on the same wafer. Film thicknesses were determined with a DekTak³ profilometer.

Exposure

Under yellow light, the sectors were exposed with a GCA-6300 10X i-line Stepper (Zeiss lens with 0.42 N.A., 10 × 10 mm field size, resolution to 0.5 µm) through a mask (features from 2 µm to 0.45 µm) with doses of 70, 175, 280, 385, 490, and 595 mJ cm^{-2}, or 280, 420, 560, 700, or 840 mJ cm^{-2} at a exposure wavelength of 365 nm, respectively. Afterwards the sectors were cut into smaller pieces and different post exposure bakes applied at 90 °C for 30 and 60 s; 100, 110 and 120 °C for each 30 s was applied.

Development

Under yellow light, the wafers were dipped into deionized water for defined time periods to determine the optimized development time. They were carefully dried with compressed air.

Characterization

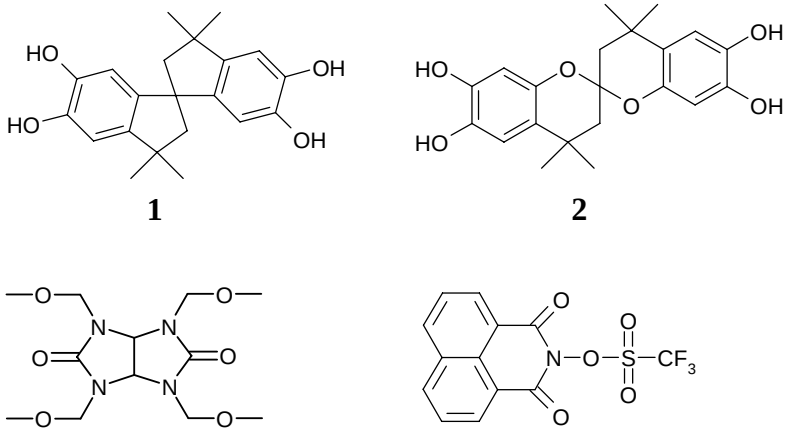
High performance liquid chromatography (HPLC, Agilent 1100 Series) analysis allowed conclusions on the water solubility, the thermal stability of the substances and the analysis of the composition of the materials after a calibration. To determine suitable wavelengths for HPLC UV detection, UV spectra of the four components were recorded on Spectrophotometer Hitachi U-3000. Triflate **4** showed two smaller maxima at 367 and 348 nm and one large maximum at 217 nm. The UV spectra of spirobisindane **1** and spirobichroman **2** are very similar. They show a large maximum (295 nm for spirobisindane, 298 nm for spirobichroman) and a smaller maximum at lower wavelengths (235 nm for spirobisindane, 238 nm for spirobichroman). For triflate a detection wavelength of 217 nm, for spirobisindane 278 nm, for spirobichroman 281 nm and for Powderlink® **3** 201 nm was chosen. The detection wavelengths of spirobisindane and spirobichroman were chosen not at the maximum

of absorption to tune the absorption intensities in the range of the less intensive PAG and crosslinker. Then measurements with each of the substances, dissolved in acetonitrile (triflate: 0.001 wt%, spirobichroman, spirobisindane and Powderlink® 0.01 wt%), was performed to determine suitable conditions and a characteristic retention times of the substances. Under the experimental conditions used, Powderlink® has a retention time of about 1.7 min, spirobisindane of about 4.91 min, spirobichroman of about 3.81 min and triflate of about 7.23 min. When the spiro samples were measured after dissolving the non-evaporated substances in pure acetonitrile, in both cases time-dependent reactions were observed. Measurement directly after dissolution resulted in detection of a large peak at the stated retention times and a smaller peak somewhat earlier. With time, the smaller peaks increased and the larger peaks decreased significantly. This indicates that a reversible autoxidation reaction took place for which 1,2- and 1,4-dihydroxybenzenes are well known in literature.[7] The suitable solution to this issue was to add a mild reducing agent which, after trials with sodium dithionite, was found to be addition of ascorbic acid. Using a solvent mixture of 60 vol% acetonitrile and 40 vol% water (containing 0.1 wt% ascorbic acid), both spiro compounds showed no time-dependent reactions. When using isocratic conditions (60 vol% acetonitrile and 40 vol% water containing five drops of concentrated sulfuric acid per liter), the retention time of ascorbic acid at 1.58 min (observable at 201 nm) interfered with that of Powderlink®. By employing a mobile phase gradient this issue was resolved. This mobile phase gradient with a flow rate of 1 mL min^{-1} started with 72 vol% deionized water and 28 vol% acetonitrile and changed in 15 min straight proportionally to 20% deionized water and 80% acetonitrile (the mobile phase contained five drops of concentrated sulfuric acid per liter). In conclusion, each HPLC run started with a detecting wavelength of 201 nm for ascorbic acid and Powderlink®, then changed at 3 min to 281 nm (for spirobisindane and spirobichromane, respectively), and at 11.3 min was switched to 217 nm (for triflate) and kept until the run was finished at 20 min. For every sample, 100 µL of a mixture of 60 vol% acetonitrile and 40 vol% deionized water (containing 0.05 wt% ascorbic acid) were used to rinse the PVD film off the wafer. This solution was then diluted with further 200 ml of the same solvent mixture. The injection volume for every sample was 25 ml. The column was a C14 ZORBAX Bonus-RP 4.6 × 150 mm, 5 mm.

The influence of the composition, the exposure dose and the time of development on the quality of the patterns was identified by comparing the resulting patterns with reflection microscope (Olympus MX50).

Results and discussion

As glass forming polyfunctional phenols, the general class of propeller-shaped spiro-type molecules which have outstanding glass-forming properties are thus interesting for our work. A literature reported glass-forming material is 6,6',7,7'-tetrahydroxy-4,4,4',4'-tetramethyl-2,2'-spirobichroman ("spirobichroman") **2** (see Scheme 1) and its derivatives which normally serve as antioxidants for polymers,[8] as a component in photographic photosensitive materials,[9] and in positive tone polymer photoresist compositions.[10] 5,5',6,6'-Tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-spirobisindane ("spirobisindane") **1** and its derivatives are used for medical[11] and photographic[12] applications as well as for positive[13] and negative[14] photoresists. Spirobisindane is insufficiently soluble in propylene glycol methyl ether acetate (PGMEA)—a typical solvent used for solvent casting of photoresist materials—for ready use as a photoresist, but is easily vapor-deposited.



1 **2**

3 **4**

Scheme 1 The investigated photoresist systems consists of three components: as matrix: 5,5',6,6'-tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-spirobisindane ("spirobisindane") **1** or 6,6',7,7'-tetrahydroxy-4,4,4',4'-tetramethyl-2,2'-spirobichroman ('spirobichroman") **2**; as acid labile crosslinker: Powderlink® 1174 **3;** and as nonionic photoacid generator (PAG): N-hydroxynaphthalimide triflate ("triflate") **4**

As crosslinker for negative tone photoresists, we have used N,N,N,N-tetra(methoxymethyl)glycoluril (Powderlink® 1174) **3**, a low molecular weight crosslinker mostly known as a curing agent in coatings and lacquers,[15] often used in combination with polyesters.[16, 17] For lithographic purposes it has served as a crosslinking reagent for etch resistant antireflective coatings as an undercoated layer for resists[18, 19] and for negative photoresist formulations containing fluoropolymers.[20] The application of Powderlink® as

utilized by our groups[6] is a key component of low molecular weight, molecular glass negative tone photoresists.

Normally, photoresist film preparation involves casting or spin-coating from low volatility solvents. Solvent-based processing may be wasteful in terms of solvent use and loss of valuable photoresist materials. Direct dry deposition of photoresist components has therefore the potential to improve both lithographic and deposition performances and to reduce process waste. Provided photoresist materials have sufficient thermal stability and a suitably low molecular weight for physical vapor deposition (PVD), this dry deposition technique may be used as a precise, environmentally friendly deposition method. As shown in studies of PVD deposition of molecular glasses for OLEDs,[21] the resulting pinhole free films (typically 10–100 nm) are very uniform and can be produced with a precise thickness and even in-depth composition gradient. Furthermore, substances that are not soluble enough for solution deposition purposes may form uniform films by PVD, thereby enabling otherwise unusable, insoluble materials to be employed as effective photoresists. A further advantage for the development of photoresist compositions is the applicability of a combinatorial PVD approach[6] which has been shown to be well suited for materials screening in studies of thin film molecular glasses for electro-optical devices.[22]

The development step of a modern photoresist, i.e. formation of the pattern, is usually performed in aqueous base solution. However, to further reduce basic waste, new environmentally friendly base-free approaches have been introduced. Development options include simple water development, quasi solventfree development with supercritical fluids like CO_2[22] or O plasma,[23] and true solvent-free development by heating in high vacuum.[24] Of the water-only developable polymer resists that have been reported in literature, examples include mixtures with novolak epoxy,[25] with carboxylic acid polymer[26] or casein–ammonium dichromate photosensitive material.[27] In addition, there are water deposit, water develop photoresists that have recently been described.[28, 29] In the studies reported here we have been able to demonstrate that as an added benefit these new PVD molecular glass photoresists are also developable in only deionized water.

In carrying out these studies we have used combinatorial PVD deposition methods and have focused on identifying resist compositions that provide superior performance. By depositing resist films with different material combinations on the same wafer, a so-called library is established to efficiently screen different compositions lithographic sensitivity, development and imaging performance where each sector is prepared under identical conditions.

In order to study the underlying questions with respect to resist composition, deposition, patterning and development, we prepared a combinatorial library as shown in Fig. 1. The library was composed of ten sectors (A–J) of different compositions. Exposing each of these sectors to six different exposure doses resulted in a combinatorial library with a total of 60 different areas. Using this library, we can rapidly assess changes in process conditions and identify particularly promising compositions coupled to optimized exposure and development conditions.

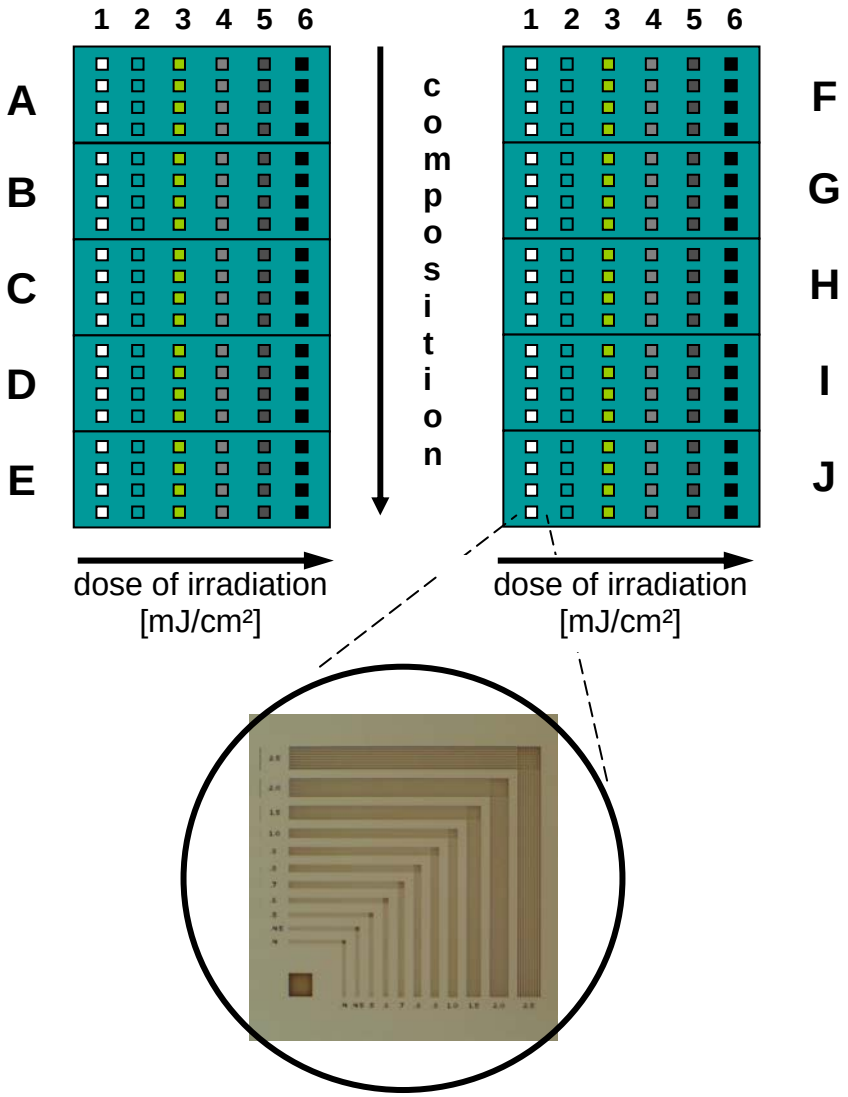


Figure 1. Representation of the combinatorial library with ten sectors A to J with different compositions of polyphenol matrix (compound **1** or **2**), the acid labile crosslinker Powderlink **3** and the non-ionic photoacid generator **4**. Each sector was exposed with 6 different doses enabling assessment of 60 different conditions simultaneously. In a sector with fixed composition and dose, it is possible we may have multiple patterns to investigate.

For the experiments, a 4 inch cleaned unprimed silicon wafer was inserted in the combinatorial PVD tool on a positionable substrate holder (see Fig. 2). In each of the three heatable sources, a quartz tube was inserted, filled with about 300 mg of Powderlink® **3**, triflate **4** and either spirobisindane **1** or spirobichroman **2**. A system of four shutters, three directly at each source and one just below the substrate, were used to adjust deposition rate and control the deposition time. A mask holder with five masks was located directly under the substrate to create sectors of controlled area. At a vacuum of about 7×10^{-6} mbar, the sources were heated individually to obtain a desired evaporation rate ratio controlled by quartz crystal sensors. When the desired composition ratio is reached, all shutters at the sources and at the substrate are opened simultaneously. During the evaporation process, the sample and mask setup itself is rotating to ensure a uniform film thickness over the entire area. After having reached a preset film thickness (~ 100 nm) as measured by two sensors near the substrate, the shutters were closed and another mask was positioned below the substrate. By changing the temperature of the sources, the evaporation rate could be set to the next composition ratio. After the appropriate ratio had been reached, the shutters were opened again and the vapor deposited on the second sector. By this sequence, the first five sectors (A–E) with different compositions were prepared. Then the substrate was rotated by 180° to allow the production of the next five sectors (F–J), so that a total of ten sectors with different compositions were obtained.

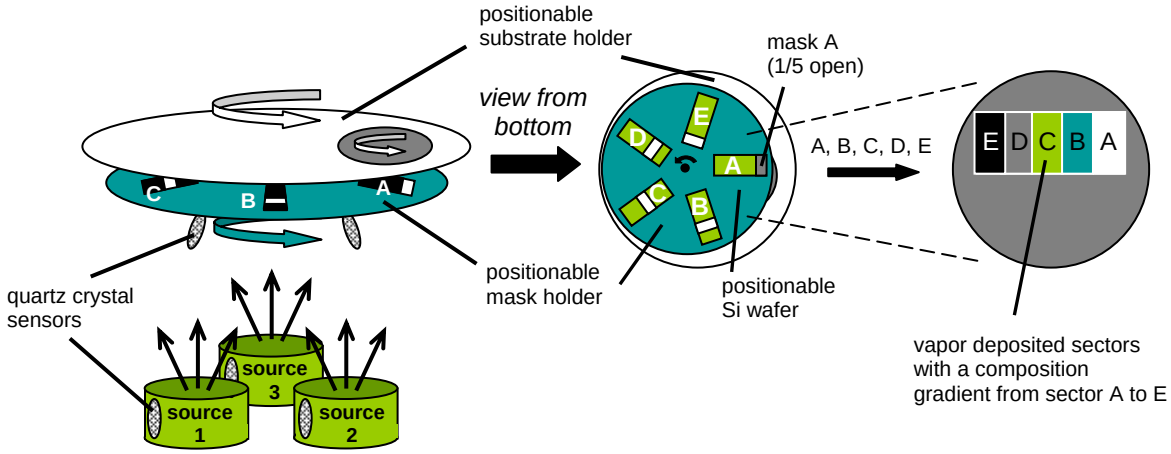


Fig. 1. Schematic representation of co-evaporation of 3 compounds by combinatorial PVD to prepare a library of sectors with different compositions. The complete setup rotates during evaporation assuring a uniform film thickness. By controlling the evaporation rate of each source, the desired composition ratio can be adjusted. The mask holder contains five different, exchangeable masks which can be selected individually. After five sectors are produced, the substrate can be rotated 180° and additional five sectors of different compositions can be prepared. Thus 10 sectors with different compositions can be prepared on each substrate.

In a vapor deposition process it must be ensured that all compounds can be deposited without thermal degradation. Vapor deposition of single component films of each of the individual compounds on 15 × 15 mm silicon unprimed wafer pieces was performed to determine their thermal stability under the evaporation conditions used. Spirobisindane **1**, spirobichroman **2**, and photoacid generator **4** were found to be vapor depositable without any detectable degradation.

After deposition coevaporated films were analyzed by HPLC (see Experimental section) and the spectra of deposited films compared with those of the unevaporated substances. In addition, a calibration of the HPLC with the used compounds, combined with thickness information derived from the quartz crystal sensors, allowed us to quantify the composition on each sector of the wafer. In prior investigations,[6] we had already confirmed the thermal stability of crosslinker Powderlink® **3** for vapor deposition. It should be pointed out that effective co-evaporation of Powderlink® can be done in combination with a polyvalent phenol. When co-evaporated, hydrogen bonds probably form with the phenolic matrix and Powderlink® is thus incorporated into the growing film.

*Photoresist system with Spirobisindane **1***

This molecular glass photoresist is composed of a photoresist matrix (spirobisindane **1**), Powderlink® photocrosslinker **3** and photoacid generator **4**. In the combinatorial experiment we varied the percentage of Powderlink® from 19.7 to 12.0 wt% (sectors A to E) and increased the percentage of photoacid generator from 2.8 to 6.5 wt% (sectors F to J), respectively. The actual compositions (1/3/4, wt%) for each sector are the following:

A 77.1/19.7/3.2; B 80.6/16.8/2.6; C81.0/15.9/3.1; D 82.9/14.6/2.5; E 84.6/12.0/2.4 and F 79.9/17.3/2.8; G 80.4/16.1/3.5; H 80.5/15.3/4.2; I 80.8/14.6/4.6; J 77.9/15.6/6.5. Each sector of the photoresist was exposed to doses of 70, 175, 280, 385, 490, and 595 mJ cm^{-2} at 365 nm. A post exposure bake (PEB) step was always performed directly after exposure. For the photoresist compositions containing spirobisindane **1** different temperatures and time periods for PEB were investigated: 90 °C for 30 and 60 s, 100, 110, and 120 °C for each 30 s. It was found that with higher PEB temperatures lower exposure doses were sufficient for creating patterns, but higher temperature may also induce more diffusion of the triflate—and thus less sharp lines. In addition, film residues were observable. Another aspect of elevated temperature PEB might be exceeding the glass transition temperature of the photoresist system which may lead to fringed lines. Ultimately we therefore used the milder conditions of 90 °C and time of 30 s for PEB.

Normally a developer consisting of 0.26 N aqueous TMAH would be used to process the photoresist, but it was found that this strength developer rapidly over developed the patterned features. Following successful studies using very dilute developer (<0.002 N TMAH) we examined water alone as developer and could resolve excellent features. Solubility investigations of the photoresist compounds were performed in pure water by HPLC, showing that Powderlink® is very water-soluble (190 g L^{-1}) whilst spirobisindane, spirobichroman and triflate photoacid generator individually are not. We believe that the amorphous nature of the film, the homogeneous distribution of the components due to the vapor deposition combined with the high solubility of Powderlink® lead to the water developability of this photoresist composition.

Using the combinatorial library we identified the composition showing the highest resolution features. From all the different compositions and conditions examined it was found that area F4 produced the most distinct, continuous lines (see Fig. 3a). Here the composition was 79.9 wt% spirobisindane, 17.3 wt% Powderlink®, and 2.8 wt% triflate. Interestingly increasing the PAG concentration and reducing the Powderlink® concentration result in patterns with lines that are no longer distinct (80.5 wt% spirobisindane, 15.3 wt% Powderlink® and 4.2 wt% triflate, see Fig. 3b). In this system, a higher concentration of PAG in the photoresist mixture leads to the process window becoming dramatically smaller.

The ratio of Powderlink® does not have such a significant influence on the pattern (not shown here). We have varied it from 12.0 wt% (Fig. 1, sector D) to 19.7 wt% (Fig. 1, sector A). Over this concentration range and using an exposure wavelength of 365 nm, sharp patterns and uniform line widths as small as 0.4 mm are observable.

*Photoresist system with Spirobichroman **2***

A very similar library for an additional molecular glass photoresist investigation was prepared by exchanging the photoresist matrix and using spirobichroman **2**. In the same manner the percentage of Powderlink® was decreased from sectors A to E and the percentage of photoacid generator increased from sectors F to J (see Fig. 1). In contrast to the first combinatorial experiment each sector of the spirobichroman **2** based photoresist was exposed in the defined areas to the higher doses of 280, 420, 560, 700, or 840 mJ cm^{-2} at 365 nm. The investigated molecular glass photoresist showed the best result at a composition of 77.6 wt% spirobichroman **2**, 20.2 wt% Powderlink® **3**, and 2.2 wt% triflate **4** using an exposure dose of 840 mJ cm^{-2} and a wavelength of 365 nm (see Fig. 3c). Due to limitations of the mask and exposure

facilities, the maximum resolution that could be realized in this photoresist system was 0.4 mm. But at a less reduced concentration of triflate **4** (1.7 wt%), the lines faded and the edges became fringed (not shown here). This indicates a low conversion of the photoacid induced reaction under these conditions, as most of the material was removed during development. One way to enhance the conversion is to increase the PEB temperature. This was realized in Fig. 3d by utilizing 120 °C for 30 s and results in no longer separated lines. This is probably due to the enhanced diffusion of the PAG at this elevated temperature and exceeding the glass temperature of the molecular glass mixture.

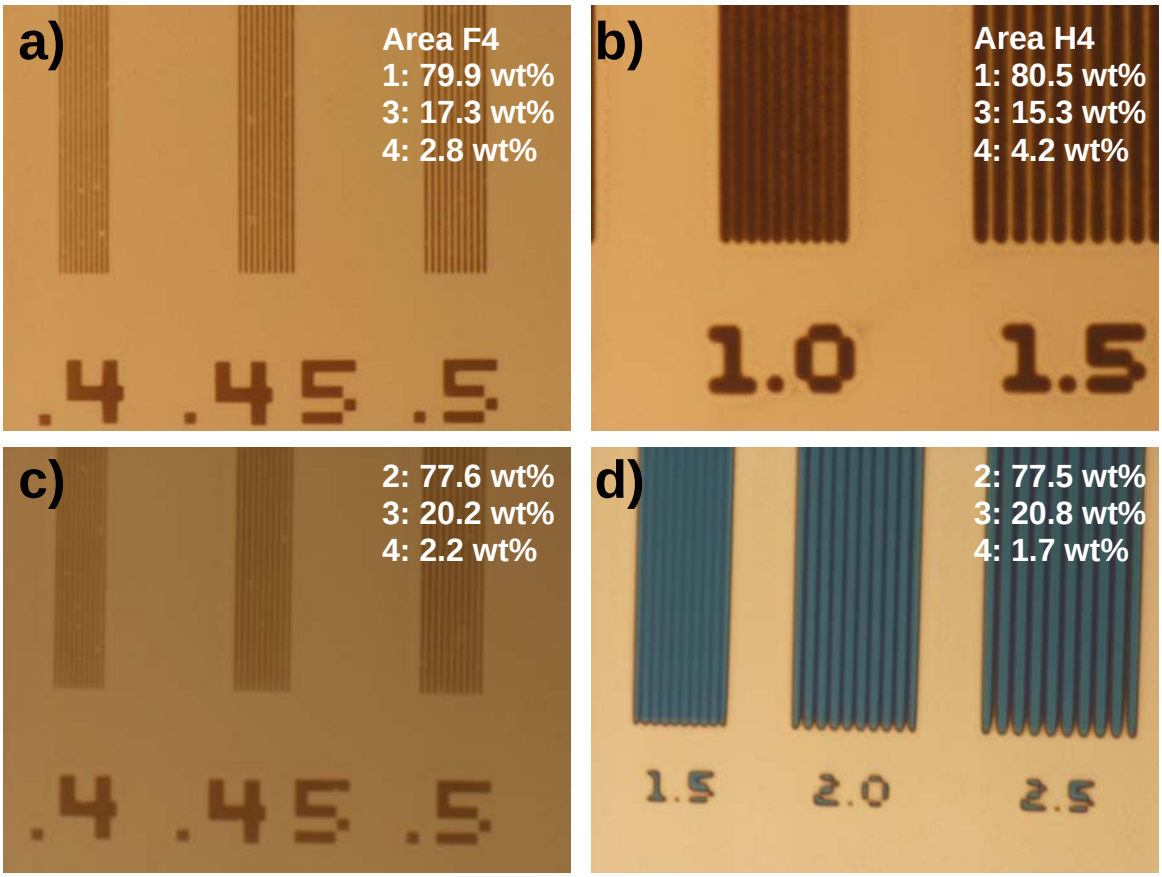


Fig. 3 Reflection microscope image (the dark lines are the exposed parts, the lighter area is the surface of the silicon wafer; the numbers indicate the line widths in microns) of (a) the optimized result with the spirobisindane photoresist. The optimized composition of 79.9 wt% spirobisindane **1**, 17.3 wt% Powderlink® **3**, and 2.8 wt% triflate **4** was exposed to a dose of 385 mJ cm^{-2} at 365 nm (area F4 in Fig. 1). After exposure and performing a PEB at 90 °C for 30 s, the wafer was dipped into deionized water for development. (b) The spirobisindane photoresist with a higher PAG percentage (80.5 wt% spirobisindane **1**, 15.3 wt% Powderlink® **3**, and 4.2 wt% triflate **4**) which was exposed to a dose of 385 mJ cm^{-2} at 365 nm (area H4 in Fig. 1). After patterning and performing a PEB at 90 °C for 30 s, the wafer was dipped into deionized water for development. The lines are not separated anymore—probably due to the diffusion of the PAG. (c) The optimized result with the spirobichroman photoresist. The optimized composition of 77.6 wt% spirobichroman **2**, 20.2 wt%

Powderlink® **3**, and 2.2 wt% triflate **4** was exposed to a dose of 840 mJ cm^{-2} at 365 nm. After exposure and performing a post exposure bake (PEB) at 90 °C for 30 s, the wafer was dipped into deionized water for development. (d) The spirobichroman photoresist (77.5 wt% spirobichroman **2**, 20.8 wt% Powderlink® **3**, and 1.7 wt% triflate **4**) which was exposed to a dose of 840 mJ cm^{-2} at 365 nm. After exposure and performing a PEB at 120 °C for 30 s, the wafer was dipped into deionized water for development. The lines are not clearly separated, propably due to the higher PEB temperature.

Conclusion

In this work we have established a new dry deposited, waterdevelopable, negative tone molecular glass photoresist containing a photoacid generator (N-hydroxynaphthalimide triflate), a crosslinker (Powderlink®) and either spirobisindane or spirobichroman as major components. Spirobisindane is poorly soluble in common spin coating solvents like propylene glycol methyl ether acetate (PGMEA). Thus film production by solvent-free physical vapor deposition is a new approach to realize photoresist films containing this substance. A combinatorial technique was employed using PVD so that sectors of different film compositions could be produced on the same wafer under identical conditions. The molecular glass resist components were co-evaporated with selected composition ratios on an unprimed silicon wafer, DUV exposed and developed in pure water. High-pressure liquid chromatography was used to verify the thermal stability of the compounds, to examine their water solubility, and, after a calibration was performed, to derive the actual composition on the silicon wafer. Combinatorial techniques, i.e. producing a compositional library on the same wafer, greatly aided the optimization of the photoresist composition and the required exposure dose. The development step was accomplished in pure deionized water. Using this new environmentally friendly process, patterns with small feature sizes of 400 nm were realized.

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Synthesis and All-Dry Lithography of Glass-Like Coumarin Derivatives

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Abstract

The paper deals with coumarin derivatives which undergo a [2+2] cycloaddition in the solid state when exposed to UV light. Several coumarin esters were synthesized for the first time using 1-(3-dimethylaminopropyl-)-3-ethylcarbodiimide hydrochloride (EDAC) with the intention to obtain thermally stable, photocrosslinkable molecules with glass-like properties and thus enhanced film forming properties. One substance is favored which meets all these requirements and is thus interesting for an approach to an all-dry, low molecular weight lithography process. The examined photoresist films were produced by physical vapor deposition (PVD), a solvent-free process. Then they were exposed to a spectral range from 320 to 480 nm through a mask to different time periods and developed in a small, heatable self-made vacuum chamber to remove the unexposed monomers by evaporation. In this way, negative tone patterns consisting of reacted coumarin derivate molecules were received by an all-dry process and without the use of other components such as a comonomer or a photoinitiator.

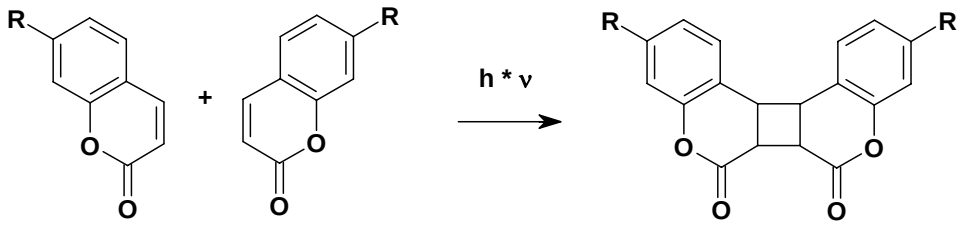
Introduction

The fabrication of smaller structures for the semiconductor industry is of great interest. Photoresists (“resists”), which are the materials that react by irradiation to form the target features in any photoresist pattern,[1] are usually based on polymers. In the last decade, it has

been shown that small molecules with glassy properties, so-called molecular glasses, can serve as resist materials as well.[2-5]

Usually, resist films needed for high resolution imaging are deposited by casting from solution. Sufficient solubility in the used solvents is a must for normal solution casting. By using solvent-free physical vapor deposition (PVD), films can be formed even from poorly soluble substances. There are several additional advantages of using PVD. The produced uniform films are very pure and can be fabricated with a precise thickness in the nanometer range. As a limitation, such materials require thermal stability and a suitable polarity—substances with only weak interaction to the substrate will desorb from its surface. This issue can be attenuated by treating the substrate surface to change its polarity. Direct deposition of photoresist materials therefore has the potential to improve deposition performance, expanding the range of film-producing molecules, avoiding the use of toxic material and for reducing process waste. Because of their small molecular size, photoresists consisting of molecular glasses are investigated as promising candidates for the next generation of photoresists.[6,7] Recently, we reported the solvent-free fabrication of low molecular-weight photoresist films via (PVD) in which various polyphenolic substances, a crosslinker and a photoacid generator were coevaporated to create different resist systems.[8,9] After exposing the wafers to different doses of 365 nm and performing a post exposure bake, the resulting patterns were developed by an aqueous basic solution and water, respectively. The final aim in our research was to avoid the use of solvents—not only for film preparation, but also for development so that no other material besides the resist itself is needed for the complete lithographic process. Coumarin derivatives are a promising material class for this goal because of they undergo a [2+2] cycloaddition when irradiated. Looking at the chemical structure of coumarin, it is closely related to cinnamic acid. In last century's early thirties a negative photo resist based on the photodimerization of cinnamic acids was one of the earliest inventions in the field of lithography: cinnamic acid derivatives were embedded in a matrix of natural film-forming resins such as copal to prevent crystallization. Later it was modified as to poly(vinyl alcohol) side chains containing cinnamic acid derivatives[10,11] to obtain a higher crosslinking yield. When exposed to UV light, cinnamic acid derivatives as well as coumarin derivatives undergo a [2+2] photodimerization in which the double bond is cleaved, and a cyclobutane ring and by this a dimer is formed (s. Scheme 1). If their sterical alignment is eligible, this even happens in solid films.[12,13] Monofunctional coumarin derivatives react to build dimers when exposed to UV light, bifunctional derivatives form polymer chains and trifunctional derivatives form networks.

Scheme. 1. Schematic sketch of a [2+2] cycloaddition of two coumarin derivatives when exposed to UV light at a wavelength above 300 nm



Coumarin occurs naturally in some plants as woodruff and different types of grasses. It is used as a scent in the perfume industry. Its anti-inflammatory properties make it useful for medicinal purposes while coumarin derivatives such as phenprocoumon and warfarin, better known as Marcumar® and Coumadin®, are interesting because of their anticoagulant properties. Regarding lithography, coumarin derivatives serve as photo sensitizer dyes for photocrosslinkable unsaturated polymers.[14-16]

The most common way in lithography to develop an exposed resist is the use of aqueous alkaline solutions. In the past, there were already researches performed to replace development solvents through such methods like so-called vapor development in which poly (olefin sulfones) were spin coated and then underwent a depolymerization when irradiated with an electron beam of 5-20 kV.[17] Other methods included Oxygen plasma,[18-20] alternative techniques used supercritical fluids like CO_2[21] or developed via x-rays.[22] Also heat-developable resists ("thermal development"), e.g. acid catalyzed depolymerizations which produce volatile monomers, are mentioned in literature.[23,24] A first all-dry lithography process was established by Sato et al.,[25] taking advantage of the thermal depolymerization of polyurea. In their work, monomers of 4,4'-diaminodiphenylmethane and 4,4'-diphenylmethanediisocyanate were evaporated, then polymerized by contact UV irradiation via a mask on the substrate. The development was performed by heating up to 300 °C in vacuum. The polymers in the exposed parts degraded slower than the oligomers in the nonexposed parts so that negative tone patterns could be produced. Residues were still observable, though. The first attempt towards an all-dry low photoresist consisting of low molecular weight molecules was performed by Mikhailovskii et al.[26] and Azarko et al.[27] Mikhailovskii vapor-deposited sulfophthaleine dyes, exposed them to UV light via a mask and developed them by heating in high vacuum. No images were provided and no data was given on residues or resolution, though. Azarko deposited carbazole derivatives in high

vacuum, irradiated them through a mask and developed the patterns by heating in vacuum at 100 to 110 °C. Again, information on residues and resolution is missing.

By irradiating a suitable amorphous coumarin derivative film through a mask, only the exposed parts react to form compounds with a higher molecular weight. The weight difference results in a change of evaporation temperature. This can be utilized to separate the exposed from the unexposed molecules—the monomers will evaporate at lower temperatures. Thus, the non-exposed material can be removed via evaporation, in contrast to the exposed parts, by heating in high vacuum. This results in negative tone patterns.

In this article we present an approach towards such an all-dry lithographic process for negative tone photoresists based on low-molecular weight coumarin derivatives.

Experimental Section

Materials and Instruments. (FP22:) 7-Hydroxycoumarin, 99%, and dimethyl aminopyridine (DMAP), 99%, were purchased from Sigma-Aldrich Co. 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDAC), 98%, was from Alfa Aesar. Dimethyl formamide (DMF) p.A. was purchased from Acros. Technical hydrochloride acid 31-33% was purchased from Hedinger. The coumarin derivatives were prepared based upon the procedure of Hassner[28] and Neises.[29] ^{1}H NMR spectra were recorded on an Avance 250 spectrometer (Bruker) using $CDCl_3$ and DMSO-d_6 as solvents. UV spectra were recorded on an Analytik Jena FLASHScan 530 spectrophotometer. The thermal properties of the products were analyzed by Mettler TGA/SDTA851 and Perkin Elmer DSC Diamond (heating rate 10 K/min, cooling rates 10 K/min or 20 K/min). The pictures of the resulting patterns were taken by microscope Leica DMRX.

Preparation of the Coumarin Derivatives (5a-5j). General procedure: 10 mmol of the acid compound, 1.5 times up to the double molar excess—regarding the acid groups—of 7-hydroxycoumarin and about 2 mmol dimethyl aminopyridine were dissolved under argon in 300 mL dry DMF. After cooling to 0 °C, a slight excess regarding the molar amount of 7-hydroxycumarin of EDAC was added, and the solution stirred for ten minutes. Then the ice bath was removed and the substances were allowed to react at room temperature for 24 h. The precipitated colorless or yellow powder was filtered and washed with diluted hydrochlorid acid (0.5 M) and deionized water until thin layer chromatography (cyclohexane-ethyl acetate 2:1 v/v plus five drops of acetic acid as eluent) showed no spot of 7-hydroxycumarin

anymore. The products were dried to give **5a-5i** as colorless powder. Yield: **5a** (85%), **5b** (74%), **5c** (79%), **5d** (40%), **5e** (52%), **5f** (74%), **5g** (63%), **5h** (76%), **5i** (55%).

Spectral data for **5a**. ^{1}H NMR (DMSO-d_6, 100 °C), δ 6.51 (d, 1H, HC=C*H*C=O), 7.34 (dd, 1H, HC-C*H*-C-O), 7.46 (s, 1H, C-C*H*-O), 7.61 (t, 1H, *H*C-CH-CH-C-CO) 7.76 (d, 1H, *H*C-CH-C-O), 7.83 (t, 2H, HC-C*H*-CH-C-CO), 8.11 (d, 1H, *H*C=CHC=O), 8.16 (d, 1H, HC-CH-C*H*-C-CO). ^{13}C NMR (DMSO-d_6, 100 °C) 109.8, 115.3, 116.6, 118.2, 128.5, 128.6, 129.1, 129.6, 133.9, 143.4, 152.9, 154.1, 159.3, 163.9. Anal. calcd. for $C_{16}H_{10}O_4$: C, 72.18; H, 3.79. Found: C, 72.01; H, 3.84. HRMS calcd. 266.05791. Found: 266.05790

Spectral data for **5b**. ^{1}H NMR ($CDCl_3$/CF_3COOD), δ 3.93 (s, 6H, 2 O=C*H*$_3$), 3.98 (s 2H, O=C-C*H*$_2$-CH), 6.67 (d, 1H, HC=C*H*C=O), 6.99 (s, 3H, arom.), 7.22 (dd, 1H, HC-C*H*-C-O), 7.28 (s, 1H, C-C*H*-O), 7.69 (d, H, *H*C-CH-C-O), 8.03 (d, H, *H*C=CHC=O). ^{13}C NMR ($CDCl_3$/CF_3COOD) 40.9, 56.0, 110.9, 112.7, 113.6, 115.0, 117.9, 120.0, 123.2, 125.7, 129.8, 146.6, 148.2, 148.6, 153.8, 154.1, 166.2, 174.1. Anal. calcd. for $C_{19}H_{16}O_6$: C, 67.06; H, 4.74. Found: C, 66.94; H, 4.35. HRMS calcd. 340.0947. Found: 340.0947

Spectral data for **5c**. ^{1}H NMR (d_6-DMSO), δ 2.97 (t, 2H, O=C-CH$_2$-C*H*$_2$), 3.47 (t, 2H, O=C-C*H*$_2$-CH$_2$), 6.49 (d, 1H, HC=C*H*C=O), 7.16 (dd, 1H, HC-C*H*-C-O), 7.23 (s, 1H, C-C*H*-O), 7.54 (t, 2H, C-CH-C*H*-CH), 7.66 (t, 1H, C-CH-CH-C*H*), 7.78 (d, 1H, *H*C-CH-C-O), 8.04 (d, 2H, C-C*H*-CH-CH), 8.07 (d, 1H, *H*C=CHC=O). ^{13}C NMR (DMSO-d_6) 28.1, 33.2, 109.8, 115.5, 116.6, 118.5, 127.9, 128.7, 129.3, 133.4, 136.0, 143.7, 152.9, 154.0, 159.6, 171.1, 198.2. Anal. calcd. for $C_{19}H_{14}O_5$: C, 70.80; H, 4.38. Found: C, 70.68; H, 4.45.

Spectral data for **5d**. ^{1}H NMR (DMSO-d_6, 100 °C), δ 6.75 (d, 2H, 2HC=C*H*C=O), 7.41 (dd, 2H, 2HC-C*H*-C-O), 7.47 (s, 2H, 2C-C*H*-O), 7.80 (d, 2H, 2*H*C-CH-C-O), 8.12 (d, 2H, 2*H*C=CHC=O), 8.46 (s, 4H, 4C*H*-CH). ^{13}C NMR ($CDCl_3$/CF_3COOD) 111.2, 115.3, 116.9, 118.1, 120.2, 130.0, 131.2, 133.6, 146.6, 153.9, 154.3, 162.6, 166.1. Anal. calcd. for $C_{26}H_{14}O_8$: C, 68.73; H, 3.11. Found: C, 68.27; H, 3.15. HRMS calcd. 454.0689. Found: 454.0689

Spectral data for **5e**. ^{1}H NMR ($CDCl_3$), δ 6.70 (d, 2H, 2HC=C*H*C=O), 7.40 (dd, 2H, 2HC-C*H*-C-O), 7.44 (s, 2H, 2C-C*H*-O), 7.76 (d, 2H, 2*H*C-CH-C-O), 7.82 (t, 1H, HC-C*H*-CH), 8.06 (d, 2H, 2*H*C=CHC=O), 8.60 (dd, 2H, *H*C-CH-C*H*), 9.08 (s, 1H, C-CH-C). ^{13}C NMR ($CDCl_3$/CF_3COOD) 111.2, 115.2, 118.0, 120.2, 129.4, 130.0, 130.3, 132.8, 136.8, 146.6, 153.8, 154.2, 162.6, 166.0, 166.1. Anal. calcd. for $C_{26}H_{14}O_8$: C, 68.73; H, 3.11. Found: C, 68.62; H, 3.03. HRMS calcd. 454.0689. Found: 454.0688

Spectral data for **5f**. ^{1}H NMR ($CDCl_3$/CF_3COOD), δ 2.13 (m, 8H, 4 O=C-CH-C*H*$_2$), 3.01 (s 2H, O=C-C*H*-CH$_2$), 6.68 (d, 2H, 2HC=C*H*C=O), 7.21 (dd, 2H, 2HC-C*H*-C-O), 7.28 (s, 2H, 2C-C*H*-O), 7.71 (d, 2H, 2*H*C-CH-C-O), 8.05 (d, 2H, 2*H*C=CHC=O). ^{13}C NMR

($CDCl_3$/CF_3COOD) 25.8, 41.3, 111.0, 115.0, 117.8, 120.2, 129.9, 146.7, 153.9, 154.2, 166.3, 176.6. Anal. calcd. for $C_{26}H_{20}O_8$: C, 67.80; H, 4.38. Found: C, 67.47; H, 4.50. HRMS calcd. 460.11582. Found: 460.11580

Spectral data for **5g**. ^{1}H NMR (d_6-DMSO), δ 1.34 (s, 6H, 2CH_3), 2.06 (t, 2H, O=C-CH_2-CH_2), 2.74 (t, 2H, O=C-CH_2-CH_2), 6.47 (d, 2H, 2HC=C*H*C=O), 7.16 (dd, 2H, 2HC-C*H*-C-O), 7.26 (d?!, 2H, 2C-C*H*-O), 7.78 (dd, 2H, 2*H*C-CH-C-O), 8.07 (dd, 2H, 2*H*C=CHC=O). ^{13}C NMR (DMSO-d_6) 24.6, 29.6, 34.2, 41.7, 110.2, 115.7, 116.8, 118.7, 129.5, 143.9, 153.1, 154.2, 159.9, 171.4, 175.3. Anal. calcd. for $C_{25}H_{20}O_8$: C, 66.96; H, 4.50. Found: C, 66.73; H, 4.52. HRMS calcd. 448.11582. Found: 448.11580

Spectral data for **5h**. ^{1}H NMR (d_6-DMSO), δ 1,30 (s, 9H, $(CH_3)_3$), 6.52 (d, 2H, 2HC=C*H*C=O), 7.40 (d, 2H, 2HC-C*H*-C-O), 7.51 (s, 2H, 2C-C*H*-O), 7.85 (d, 2H, 2*H*C-CH-C-O), 8.11 (d, 2H, 2*H*C=CHC=O), 8.44 (s, 2H, C-CH-C-C-tButyl), 8.64 (s, 1H, C-CH-C). ^{13}C NMR (DMSO-d_6) 30.2, 34.2, 101.7, 109.4, 115.0, 116.4, 117.8, 127.8, 128.7, 129.1, 131.0, 142.9, 152.4, 153.7, 158.8, 162.9. Anal. calcd. for $C_{30}H_{22}O_8$: C, 70.58; H, 4.34. Found: C, 70.42; H, 4.36. HRMS calcd. 510.1315. Found: 510.1314

Spectral data for **5i**. ^{1}H NMR (DMSO- d_6, 100 °C), δ 6.45 (d, 3H, 3HC=C*H*C=O), 7.39 (d, 3H, 3HC-C*H*-C-O), 7.47 (s, 3H, 3C-C*H*-O), 7.82 (d, 3H, 3*H*C-CH-C-O), 8.04 (d, 3H, 3*H*C=CHC=O), 9.05 (s, 1H, C-CH-C). ^{13}C NMR (DMSO-d_6 at 100 °C) 109.5, 115.2, 116.6, 117.8, 128.9, 130.3, 134.8, 142.9, 152.2, 153.8, 158.8, 162.0. Anal. calcd. for $C_{36}H_{18}O_{12}$: C, 67.30; H, 2.82. Found: C, 62.81; H, 3.05. HRMS calcd. 642.07983. Found: 642.07980.

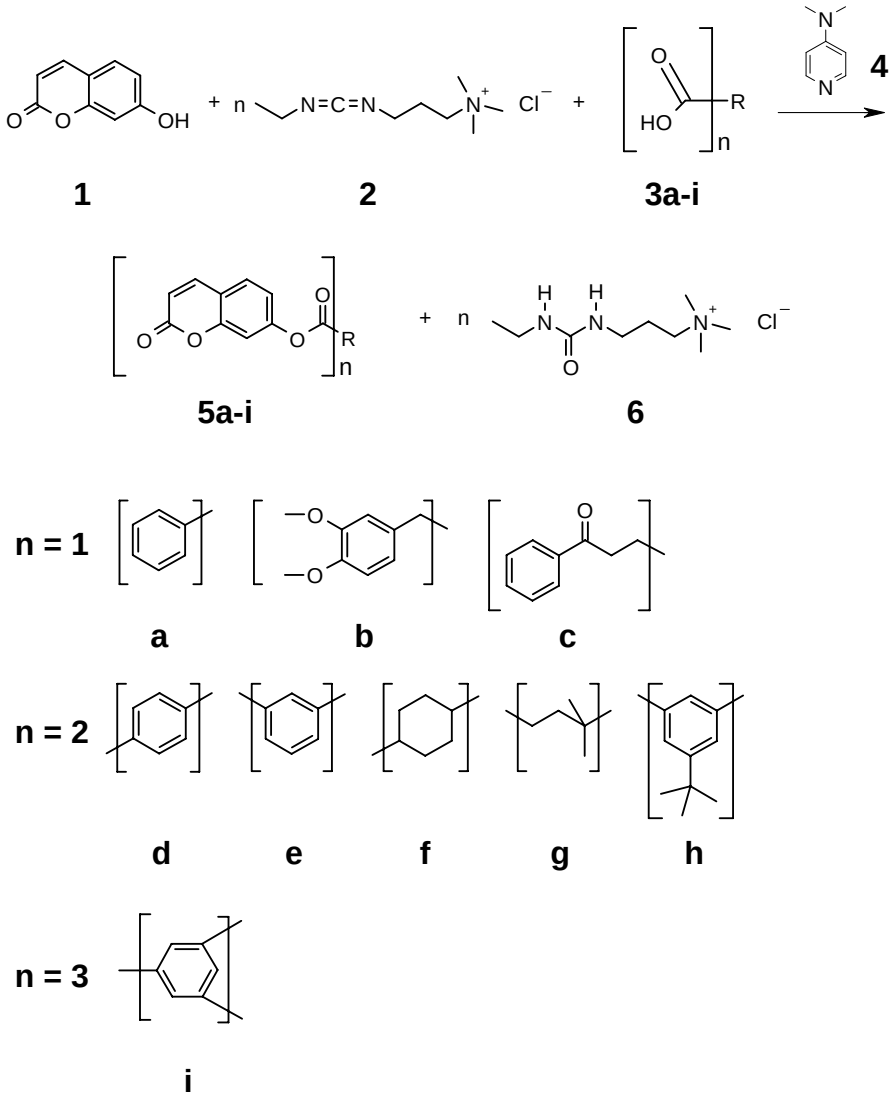
Physical Vapor Deposition, Exposure, Development and Characterization. The resist films were prepared by physical vapor deposition (PVD) which was performed with Balzers PLS 500 at a pressure of 7×10^{-6} mbar. Non-primed quartz plates were used as substrates for UV spectroscopy with an Analytik Jena FLASHScan 530 spectrophotometer. For conducting patterned imaging, 4 inch silicon wafers (110 orientation), cleaned with aceton and isopropanol, were employed as substrates. Film thicknesses were determined with a DekTak³ profilometer. The films were exposed for defined times through a mask in hard contact mode with Mask Aligner EVG 620 with a mercury lamp (40mJ/cm²) using dielectric mirror type C, providing an irradiation spectrum of about 320 to 480 nm. The mask is made from quartz glass and provides patterns with several line widths from 10 µm to 1 µm. These patterns exist as features which let the light through the mentioned sizes and as inversed patterns in which the lines are nonpermeable, but the rest is. The exposed wafers were cut into smaller pieces and heated in high vacuum at different temperatures from 80 °C to 320 °C for various times (1 min to 15 h). For this, one half of the development facility—a self-made flat

small vacuum chamber—was put onto a precision hot stage (Figure 2). The second half was cooled by being situated onto a brass block which was placed in an ice bath. The wafer piece was placed in the cooler half until the heated side has reached a constant temperature and the vacuum was at about 1×10^{-4} mbar. Then the wafer was slid into the heated half by tilting the facility quickly. After the defined time has passed, the wafer was slid back into the cooled half. The quality of the resulting patterns is judged by observing the wafer pieces with reflection microscope Leica DMRX. The thermal characterization was performed on Mettler TGA/SDTA851 and Perkin Elmer DSC Diamond (heating rate 10 K/min, cooling rates 10 K/min or 20 K/min).

Results and Discussion

Synthesis of Coumarin Derivatives. We synthesized different esters containing one, two or three coumarin units connected to an aromatic or aliphatic core. The general synthetic route, using 7-hydroxycoumarin **1**, 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDAC) **2**, and dimethylaminopyridine (DMAP) **4**, is shown in Scheme 2. To enhance the glass-forming properties of the coumarin derivatives, bulky groups were introduced or asymmetric molecules were synthesized. Since the size can have influence on the thermal stability, their molecular weight must not be too big.

Scheme 2. General reaction scheme and overview of the synthesized coumarin derivatives



Except for the monofunctional **5a**, standard esterification procedures like using **1** and the favored acid chloride in the presence of pyridine[30] failed. No product or a too complex mixture of product and byproducts was formed. Since some of the target materials are only poorly or not soluble in any standard organic solvent, purification trials failed. After several unsuccessful experiments with different solvents and reagents, carbodiimides were found to be qualified for preparing these coumarin derivatives. The most common carbodiimide reagent, dicyclohexylcarbodiimide (DCC), was not suitable, though, because the by the esterification process formed urea derivative is poorly soluble—as are some of the products, too. Thus the separation turned out to be too complex and time-consuming. A more convenient way was found by using a different carbodiimide, 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDAC) **2**. This reagent and its urea are water-soluble and thus can be easily removed by washing with water, allowing the synthesis of all the herein

presented new coumarin derivatives since they are not or only poorly water-soluble. The reactions were all accomplished under argon atmosphere because of the water-sensitivity of the carbodiimide. In each reaction, 7-hydroxycoumarin **1** was applied in excess to the functional acid groups **3a-i**. EDAC **2** served as esterification agent and dimethyl aminopyridine (DMAP) **4** catatalyzed the reactions.

Thermal Characterization. For the presented all-dry lithographic process, useful substances must be thermally stable for the film preparation by vapor deposition. To serve as photoresist materials, they should additionally give amorphous films after evaporation onto the substrate. To examine their thermal properties, the substances were tried to be sublimed as well as characterized by thermal gravimetric analysis (TGA) and difference scanning calorimetry (DSC). The results are presented in Table 1. Three substances (**5b**, **5g**, and **5h**) show a glass transition temperature which implies glass-forming properties.

Table 1. Thermal characterization of the synthesized coumarin derivatives

substance	**T_m [°C]**[a]	**$T_{onset,-5\%}$ [°C]**[b]	**weight loss [%]**[b]	**subli-mable?**	**amorphous film?**	**T_g [°C]**[a]	**T_{rc} [°C]**[a]	**T_c [°C]**[c]
5a	165	126	100	yes	no	-	-	137
5b	122	265	90.4	yes	no	15	80	-
5c	222	170	96.7	no	-	-	-	195[f]
5d	381	222	79.9	yes	no	-	n.d.[e]	n.d.[e]
5e	355	380	75.6	yes	no	-	-	276
5f	289	306	90.2	no	no	-	-	266
5g	139[d]	320	100	yes	no	25	-	-
5h	263	415	78.4	yes	yes	88	151	-
5i	300	341	71.4	no	-	-	-	206

T_m: melting point; $T_{onset,-5\%}$: weight loss of 5%; T_g: glass transition temperature;

T_{rc}: recrystallization temperature; T_c: crystallization temperature

a) measured by DSC (2^{nd} heating, 10 K/min)

b) TGA (30-650 °C at 10 K/min, under argon)

c) DSC (1^{st} cooling, 10 K/min)

d) DSC (1^{st} heating, 10 K/min), no T_m at 2^{nd} and 3^{rd} heating

e) Not determinable

f) Observation with polarization microscope (heating/cooling rate 5 K/min)

After performing prescreening experiments with the various synthesized derivatives in a sublimation apparatus, it was found that **5c**, **5f**, and **5i** decompose when heated and are thus not suitable for evaporation. **5a** is thermally stable during sublimation. Under the evaporation conditions used in this work (pressure of 7×10^{-6} mbar, substrate at room temperature), the substance desorbs readily from the substrate, though, and thus no film could be produced. It is supposed that the interactions between the material and the surface of the substrate are too weak. Physical vapor deposition might still be possible if the substrate is cooled. No glass transition temperature (T_g) was found in DSC for **5a** when heated and cooled in the range of -20 °C to 180 °C at 10 K/min which indicates crystallinity. **5b**, **5d**, **5e,** and **5g** are also stable during sublimation. They can be vapor deposited, but the resulting films are crystalline which is already indicated by a missing (**5e**) or a very low T_g (**5b**: 15 °C, **5g**: 25 °C), respectively, in DSC. This fact makes them less interesting for lithography purposes. **5h** can be sublimed and is thermally stable up until 348 °C under N_2 atmosphere ($T_{onset,-5\%}$: 415 °C; both temperatures measured by TGA). Physical vapor deposition is possible and the film produced by PVD is amorphous. It has a relatively high glass transition temperature of 80 °C. It seemed well suitable for our purposes and was therefore used for further all-dry lithographic experiments.

Physical Vapor Deposition (PVD). Instead of casting from solution, our resist films were prepared solvent-free by PVD at a pressure of 7×10^{-6} mbar. This was performed on quartz plates for UV measurements and on silica wafers for patterning. To evaporate the material, about 300 mg is put inside a quartz tube into the so-called source of the PVD chamber. Up to three substances can be evaporated simultaneously.[31] After a constant vacuum is reached, one or several sources are heated to evaporate the material. The vapor deposits onto the substrate, which is situated about 35 cm above the sources, to give a solid film. The substrate is positioned in a rotating setup in order to receive smooth surfaces with a uniform layer thickness. Quartz sensors are situated at each of sources and below the substrate to track evaporation rates and film thicknesses. The preparation of negative resist films by PVD is described in detail in other publications of ours.[8,9] The film thickness of the investigated films typically ranged from 150 to 300 nm. The evaporation of **5h** as well as a coevaporation of **5g** and **5h** resulted in amorphous films. The mixture crystallized about two hours after finishing the evaporation, though, while a film of **5h** remains amorphous for at least two weeks (controlled by polarization microscope). Thus, the mixture is not suitable for the application as a photoresist, and lithographic investigations focused on **5h**.

Exposure Time. As monomers, two maxima at about 280 nm and 315 nm, which result of the absorption of the double bound, are visible in the UV spectrum of coumarin derivatives. The photodimerization (the formation of a cyclobutane ring caused by exposure) is an equilibrium reaction. Below 300 nm, the monomers reform.[32] Thus, a wavelength spectrum from 320 to 480 nm (maximum at 365 nm) was used. However, the spectra of the lamp and of the coumarin derivative only barely overlap which results in long exposure times. The progression of the cleavage of the double bonds can be traced by UV spectroscopy. The related maxima at 280 and 315 nm decrease with time while the maximum at about 240 nm increases due to a change in the aromatic chromophore system. For an efficient establishment of a photolithographic process, the optimal exposure time has to be determined. For that, **5h** was vapor-deposited on a quartz plate, then the produced 300 nm thick film was exposed to the described wavelength spectrum for various times, ranging from 5 to 50 min. After 5 min of irradiation, the characteristic maxima are still very prominent, while after 50 min of irradiation, they are nearly vanished (see Figure 1). This indicates that the ratio of the formed dimer is very low after 5 min, while after 50 min, the [2+2] cycloaddition is nearly completed. Therefore the time for the later following exposures through a mask was set to 50 min.

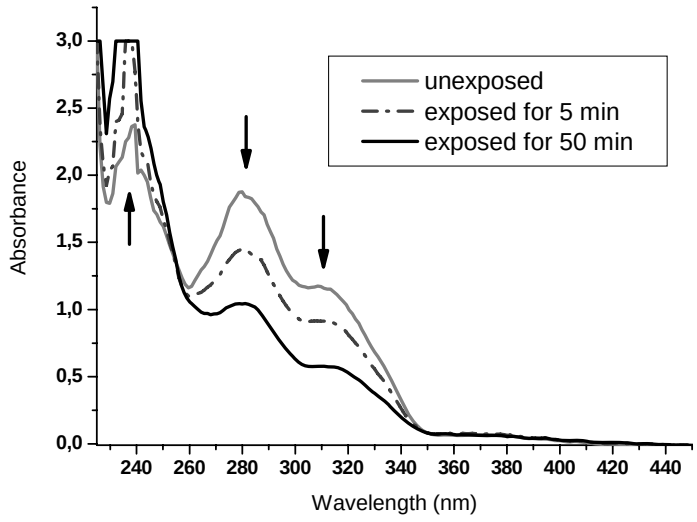


Figure 1. *UV absorption spectra of a 300 nm thick film of coumarin derivative* ***5h****, prepared by evaporation on quartz glass, unexposed (light grey line), irradiated for 5 min (dashed grey line) and 50min (black line). The two maxima at a wavelength of about 280 and 315 nm result from the absorption of the double bond. They decrease by exposure time while the maximum at 240 nm increases, indicating that the cleavage of the double bond and thus the [2+2] cycloaddition takes place.*

Exposure, Development and Patterns. In a second experiment, a 150 nm thick film of **5h** was prepared by PVD on an unprimed silicon wafer. For the investigation of the influence of the exposure time, this film was irradiated with EVG mask aligner for 15 and 50 min, respectively, through our mask. The wafers were broken into pieces of about 1.5 cm × 1.5 cm which were put into the above described vacuum development facility shown in Figure 2 for several defined times from 1 min, 2 min, 5 min, 15 min, 30 min, 60 min, 2 h, and 5 h to 15 h and temperatures from 80, 85, 100, 110, 120, 160, 160, 200, 240, and 280 to 320 °C under high vacuum.

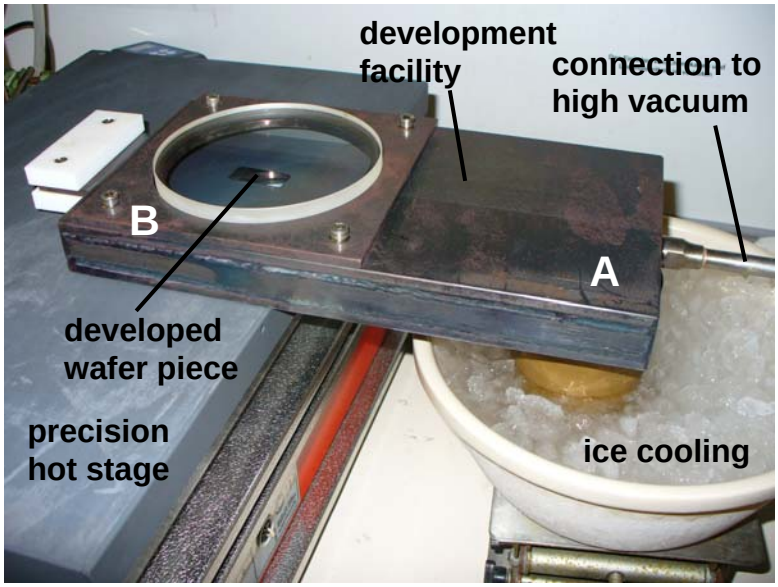


Figure 2. *The exposed wafers are broken into pieces and are developed in the self-made development chamber which is set under high vacuum. The glass opening is covered to avoid incidence of light. One side of the facility is cooled by being positioned on a brass block which is placed in an ice bath (A), the other side is situated on a precision hot stage (B). The wafer piece is inside the vacuum chamber and first on the cooled side. When the vacuum is constant and the heated side has reached its final temperature, the wafer piece is slid over to the heated side by tilting the facility. The monomer evaporates while the exposed patterns remain on the surface. In this way the patterns are developed by evaporation.*

The resulting patterns on the wafers pieces were observed by reflection microscopy. It was found that, depending on time and temperature, the produced features differed in line continuity, feature sharpness, and residues. A exposure time of 15 min is too short for a sufficient photodimerization rate. No continuous lines were observed at a development time of 1 min at 280 °C, probably because too many monomers remained in the exposed parts and were thus removed by the development procedure. When the photoresist film was exposed to 50 min and developed the same development conditions, more continuous patterns were

observed (see Figure 3a and b). But the quality of the patterns of **5h** were still more increased after an exposure time of 50 min and a development under vacuum at 120 °C for 15h. The invers line pattern (see Figure 3c) showed continuous lines and no residues were observable. But wherever larger areas of unexposed monomers have to be removed by heating in high vacuum, crystallization took place. These crystals could not be removed by the used vacuum development conditions. It was demonstrated, though, that an all-dry photoresist on the base of coumarin derivatives could be realized by vapor deposition of the monomers, exposure through a mask and development by heating under high vacuum.

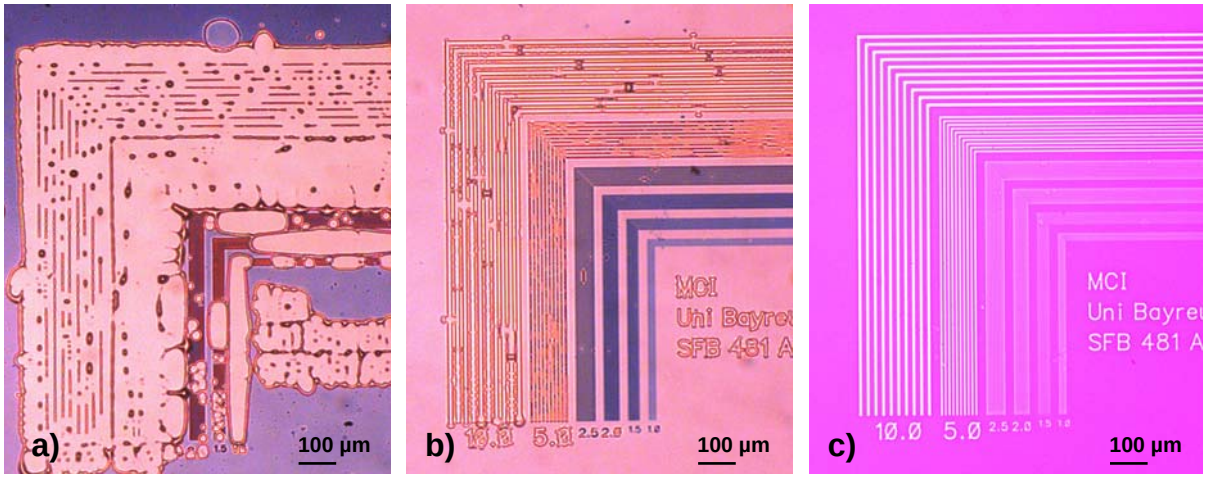


Figure 3. *Reflection microscope images of inversed patterns (darker areas are the exposed parts), produced on 150 nm thick films of* ***5h****, prepared by PVD and*
a) exposed to 15 min, developed at 280 °C for 1 min,
b) exposed to 50 min, developed at 280 °C for 1 min,
c) exposed to 50 min, developed at 120 °C for 15h.

Conclusion

This work describes a promising new way to employ low molecular glass-like coumarin derivatives in the field of all-dry lithography. Three of nine (of which eight are newly synthesized) coumarin esters can be vapor deposited and thus used for the solvent-free layer fabrication process on a substrate. Two of these three crystallize, while one derivative forms an amorphous film on the substrate and was investigated in detail for photolithography. When exposed to UV light above 300 nm, the ester photodimerized. This was tracked by UV spectroscopy. Patterns of a mask-exposed coumarin derivative were developed by heating under high vacuum to evaporate unexposed monomer. Different development temperatures and times were investigated, and the resulting patterns were observed by reflection microscopy. Optimized conditions were determined to be 50 min of exposure time and a

development at 120 °C for 15 h under high vacuum. Continuous lines without any residues were obtained; crystals were observed in larger areas, though. Under the described conditions, clear negative tone patterns could be produced successfully.

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All-Dry Processing of a Negative Tone Photoresist based on a Low Molecular Weight Coumarin Derivative**

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Advanced Materials, intended for submission

High resolution patterns are a basic requirement for the electronic devices we use in our daily life. The need for ever smaller features actuates the research in this field regarding resist materials and employed techniques. Whilst light wavelength is a natural limit to the resolution when produced by photolithography, speed remains a vital argument for this method of patterning. Special designed optical pathways allow now pattern sizes up to 32 nm and thus molecule dimension comes to the focus of investigations.[1] A few years ago, it was shown that the normally used polymers in resists can be replaced by low molecular weight materials which show glass-like properties, known as molecular glasses.[2] By utilizing these materials, line edge roughness should be reduced. Molecular glasses can be employed e.g. as components in chemically amplified resists (CARs).[3] By exposing the CAR to UV light, an acid is generated from a photoacid generator (PAG).[4] The formed acid molecules catalyze a reaction of the other component or various components of the resist, e.g. a deprotection or a crosslinking reaction, during a post exposure thermal treatment.[5,6] The acid molecules diffuse to a greater or lesser extent. Due to this diffusion, the acid-catalyzed reactions may also take place in adjoining non-exposed regions. This can be troublesome regarding resolution and line edge sharpness. Additionally, the composition of such a photoresist

system, consisting of at least two components, has to be optimized. Therefore, a molecular glass that reacts with itself when irradiated is interesting for investigations. Many coumarin derivatives are known to undergo a [2+2] cycloaddition to give a dimer when exposed to UV light in solution[7,8] and in solid state,[9,10] although not every derivative reacts by dimerization.[11,12] It is important to bear in mind that coumarin derivatives should only be exposed to wavelengths above 300 nm, otherwise the generated dimers cleave and monomers will be preferentially reformed.[13] By using those low-molecular weight photoresist materials for lithography, new film deposition techniques like deposition from vapor state are accessible.[14] The suitability of physical vapor deposition (PVD) for producing patternable photoresist films was shown by us, the exact procedure is described elsewhere.[15] By using this coating method, the deposition performance can be improved e.g. by creating subsequent film layers or gradients in film thicknesses. Additionally, waste will be reduced and patterns from hardly soluble substances are possible to be produced. Regarding the solvent-free film fabrication, up to three substances can be coevaporated in high vacuum and deposit onto a rotating substrate. The resulting films are very pure and uniform in composition and film layer thickness, which can be precisely produced in the nanometer range. However, suitable materials must not decompose under the conditions of evaporation and a sufficient interaction between the evaporated substance and the surface of the substrate is necessary to prevent desorption in vacuum. The evaporation of monomers in high vacuum cannot only be used for the preparation of the photoresist film, but also for the development of the patterns by desorption of the non-exposed material via thermal treatment under high vacuum. By doing so, a solvent-free photolithography is possible. Such an all-dry approach to photoresists was performed by Sato et al.[16] His group vapor-deposited monomers of 4,4'-diaminodiphenylmethane and 4,4'-diphenylmethanediisocyanate, then high molecular polyurea was generated by irradiating through a mask. The development was performed by heating under high vacuum and took advantage of the slower degradation of the polymers in the exposed parts compared to the evaporation of the monomers in the non-exposed parts. But residues were still observed at the non-exposed parts resulting from the thermal induced polymerization. A solvent-free processing of patterns from low molecular weight material is also literature known.[17] For this, sulfophthaleine dyes were evaporated, exposed and developed in high vacuum by Mikhailovskii et al. No further details were given on residues or the achieved resolution, though. Recently, newly synthesized coumarin derivatives have been proven by us to be qualified in general for an all-dry low molecular weight photolithography process, but showed crystalline structures in the unexposed parts after developing by thermal

treatment under high vacuum.[18] In this work, we present an improved approach to a self-reacting coumarin derivative photoresist which can be applied in an all-dry photolithography. A new coumarin derivative which forms dimers when exposed to UV light was synthesized. It is thermally stable so that a film can be produced solvent-freely by PVD. The resist film was exposed to UV light through a mask to replicate its patterns on the photoresist. After evaporating the unexposed monomers by thermal treatment under high vacuum, no crystals and no residues were observed by optical microscopy. A relatively harmless, vapor-depositable sensitizer was found to reduce the necessary exposure time significantly. The necessary steps of such an all-dry fabrication of a molecular glass photoresist are shown in Scheme 1.

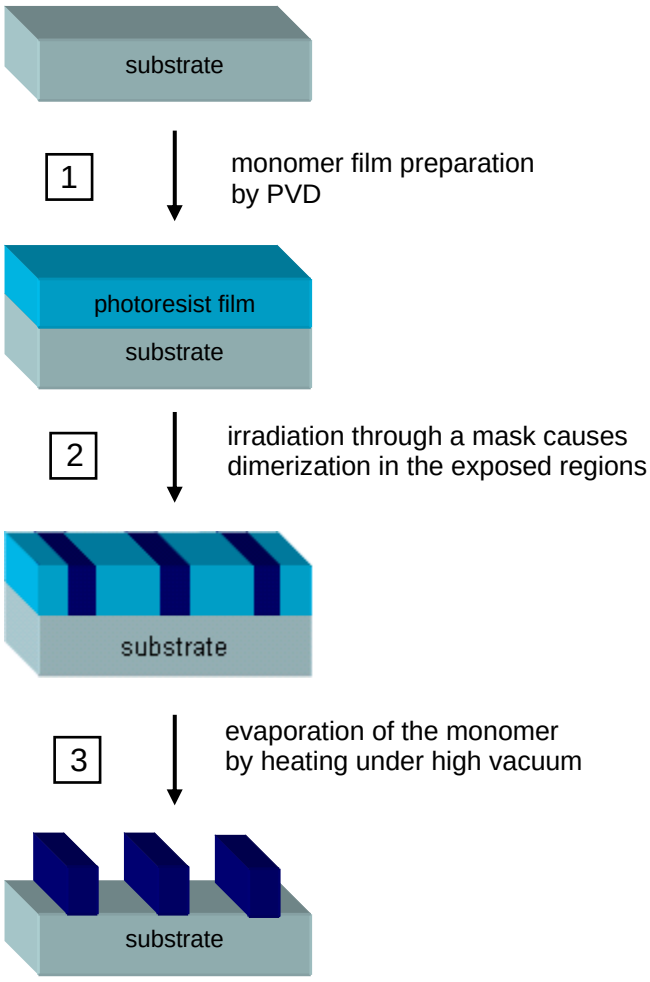
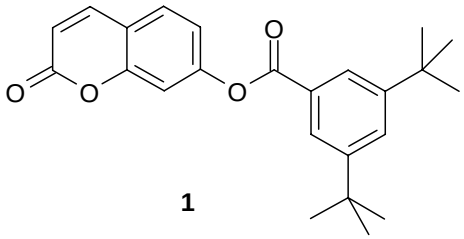


Figure 1. Scheme for the all-dry preparation of a low molecular weight negative tone pattern. 1: A film in the thickness range of 30 to 300 nm of the newly synthesized coumarin derivative is prepared by PVD. 2: The photoresist film is then exposed to various doses of UV irradition above 300 nm through a mask. During exposure, the monomers react to form dimers. 3: When thermally treated under high vacuum, the dimerized molecules remain on the substrate while the unexposed monomers evaporate and thus are removed. For decreasing the exposure time, a sensitizer can be coevaporated with the coumarin derivative.

The synthesized and characterized 3,5-Di-tert-butylbenzoiccoumarinester **1** (Scheme 1) was evaporated at 7×10^{-6} mbar onto a quartz glass substrate as film. To study the influence of the irradiation dose, UV spectra at defined spots were measured after varying the exposure time from 0 min to 50 min to a lamp with a spectrum from 330 to 480 nm (40 mW/m^2 at 365 nm). and compared to those of the same, previously unexposed, sectors. The decrease of two characteristic peaks at about 280 nm and 315 nm which correspond to the double bound of the monomer was clearly observable. This indicated the formation of a cyclobutane ring und thus the dimerization. Even at the extremely long exposure time of 50 min, the maxima decreased further which showed that the reaction is still not completed. The reason for the slow reaction rate is the barely overlapping spectra of the lamp and the UV absorption spectra of the coumarin derivative which exhibits nearly no absorption above 350 nm.

To increase the sensitivity of the coumarin derivative, a vapor-depositable sensitizer was investigated. For resists consisting of cinnamic derivatives, several sensitizers are known[19] to improve the quantum yield by providing a more overlapping spectrum with the typical spectrum of a mercury lamp (maximum at 365 nm). They are able to pass the absorbed energy to the cinnamic derivatives, and by this, exposure doses can be significantly reduced. To improve the irradiation step towards shorter exposure times, the coevaporation of a sensitizer with **1** was considered. Except for benzophenone, which should be unsuitable for PVD because of the low melting point of 45 °C, all sensitizers for cinnamic derivatives mentioned in literature[19] are toxic and/or cancerous, though, like the highly effective Michler's ketone **2a**. A very similar molecule, Michler's ethyl ketone **2b**, is less harmful and should have a similar sensitizing effect because of the identical core (Scheme 1).



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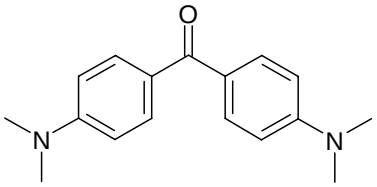
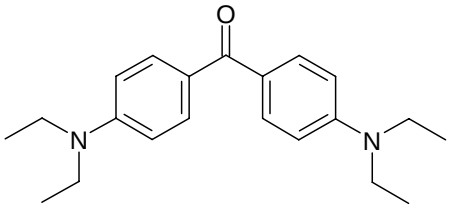


2a



2b

Scheme 1. Chemical structures of the synthesized coumarin derivative 3,5-Di-tert-butylbenzoiccoumarinester **1**, and the purchased sensitizers Michler's ketone **2a** and Michler's ethyl ketone **2b**.

To reduce the exposure doses, the coumarin derivative was coevaporated with about 10 wt.% of **2b** on a quartz plate. Then, the UV spectra were measured and compared with those of an unexposed unsensitized film of **1**. The expanded spectrum towards longer wavelengths, prolonged to 400 nm, confirmed the efficient coevaporation. After that, the sensitized film of **1** and **2b** was exposed at defined spots to a different exposure time, ranging from 2 sec to 50 min. The obtained UV spectra of unexposed spots and of those which were exposed to 5 min were plotted to those of the unsensitized unexposed and 5 min exposed film of pure **1** (Fig. 2). It can be clearly seen that the double bond maxima in the sensitized film decrease much faster (black arrow) than those in the unsensitized film (grey arrow). After 5 min of exposure, the maxima of the sensitized film were nearly completely vanished while they are still clearly visible in the unsensitized film, even after 50 min. This shows that Michler's ethyl keton **2b** is a very efficient sensitizer for the coumarin derivative **1**.

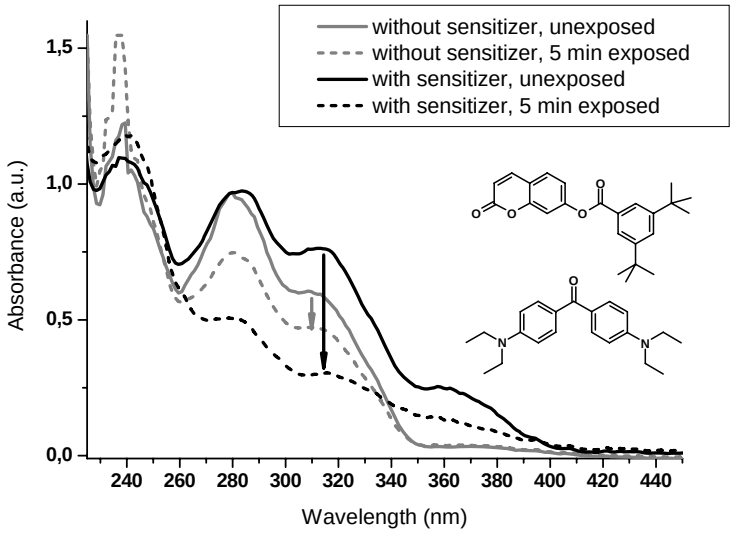
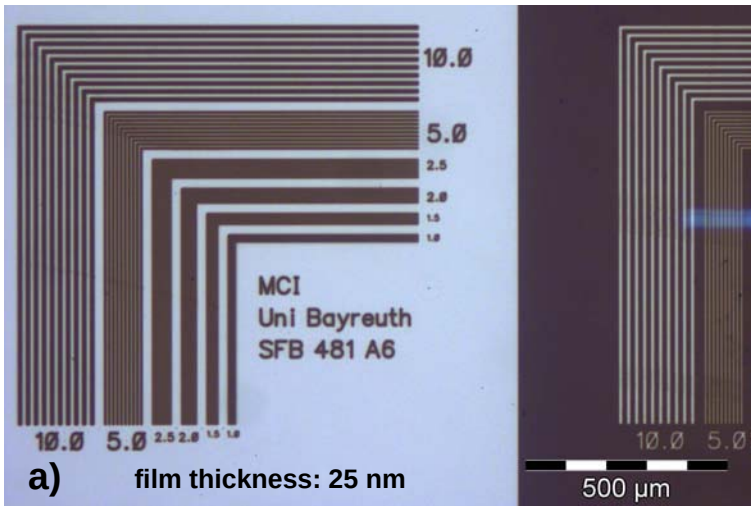
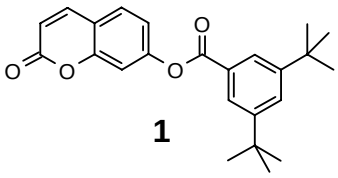


Figure 2. UV absorption spectra of **1** with and without Michler's ethyl ketone **2b** on quartz plates before and after 5 min of exposure. The unexposed coumarin films (film thicknesses about 300 nm, prepared by PVD) show the typical absorption maxima of the double bound at about 280 nm and 315 nm (solid lines). When exposed 5 min to the mercury lamp of the mask aligner (providing irradiation of 330 to 480 nm), those characteristic maxima decreased because of the photoinduced cleavage of the double bonds and the formation of cyclobutane rings. The UV spectrum of the sensitized film before exposure (solid black line) shows the extended absorption spectrum, finishing at 400 nm instead of 350 nm, which provides an increased overlap with the spectrum of the UV lamp. The maxima of the sensitized coumarin derivative decreased significantly more (black arrow) in the same time than the unsensitized film (grey arrow). This demonstrates that the coevaporation was successful, that **2b** is a suitable sensitizer for **1** and that it reduces the necessary exposure dose significantly.

For producing patterns on a substrate, **1** as well as **1** in a mixture with **2b** were prepared PVD with a layer thickness of 25 and 90 nm respectively, onto a solvent-cleaned Si wafer. Suitable exposure times were derived from the UV spectra. Thus, the film of **1** was exposed to 5 and 50 min and the film of coevaporated **1** and **2b** was exposed to 10 s and 5 min. The different exposure times were realized with a mask which provided structures with line width from 10 to 1 µm. The solvent-free development was performed in a self-made high-vacuum development facility. The increase of the molecular weight—and thus a higher melting point—when photodimerized lets the exposed parts remain on the substrate while the unexposed monomers evaporate during thermal treatment under high vacuum. To realize this solvent-free development by a well-defined thermal treatment, one half of the flat development chamber was situated on a precision hot stage, the other half was cooled by being positioned on a brass block which stood in an ice water bath. For the development, the exposed wafers were broken into smaller pieces. Single pieces were put into the development

chamber and situated in the cooled part. Then the hot stage was set to the defined temperature and high vacuum was applied. When the temperature and the vacuum were equilibrated, the wafer piece was slid into the heated half by tilting the chamber. After the defined development time has passed, the wafer piece was moved back into the cooled half. The resulting patterns, out of many experiments differing in exposure time, film thickness, development temperature and time, were observed by optical microscopy. It turned out that even though the UV spectra of **1** and **2b** when exposed to 10 s showed a significant decrease of the relevant maxima, nearly no patterns on the samples irradiated for this short time were observable. Comparing the patterns from **1** to that from coevaporated **1** and **2b** when each irradiated 5 min, it was clearly observable that a development time of 5 min was too short for **1** to produce patterns of continuous lines, but for coevaporated **1** and **2b**, under these conditions clear features were obtained. The quality of the resulting patterns of coevaporated **1** and **2b** after 5 min is quite similar to those of **1** exposed to 50 min. This demonstrates the effectiveness of **2b** as a suitable sensitizer for **1**. Regarding development conditions, the temperature should not be set below 70 °C to evaporate the monomer but also not above 100 °C. In the first case, nearly no monomer evaporated whilst in the latter case the structure-forming dimers seemed to melt. The lower the temperature is, the longer the wafer pieces have to be developed under high vacuum. 30 min at 100 °C was the shortest time tested in which patterns could be observed. Clear patterns were achieved by setting the temperature to 80 °C and developing the pattern over night, i.e. about 15 h under high vacuum. By comparing the line edge roughness in obtained patterns of films of coevaporated **1** and **2b** prepared with different film thicknesses, a strong dependency on the thickness was observed. Keeping all other parameters (exposure time, temperature and time of development) the same, it was observable that the thicker the film was (up to 150 nm), the more molten the features appeared. This is illustrated in Figure 3b (90 nm thick film of coevaporated **1** and **2b**, 5 min exposure time, development under high vacuum at 80 °C for 15 h). Non-softened lines were only obtained in film thicknesses below 30 nm (Fig. 3a, 25 nm thick film of coevaporated **1** and **2b**, same parameters as stated for 3b). The reason for this behavior might be that the glass transition temperature (T_g) of the dimer depends on the film thickness–the thicker the film, the lower T_g which leads to softening while development above certain film thicknesses. The reversed thickness dependency of T_g in thin films is discussed in literature for amorphous polymers regarding the influence of microstructure[20] and substrate materials such as Al versus Si.[21] Additionally, residues could be observed on the thicker films while the thinner films did not show residues.





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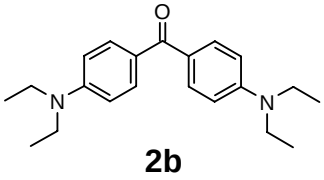
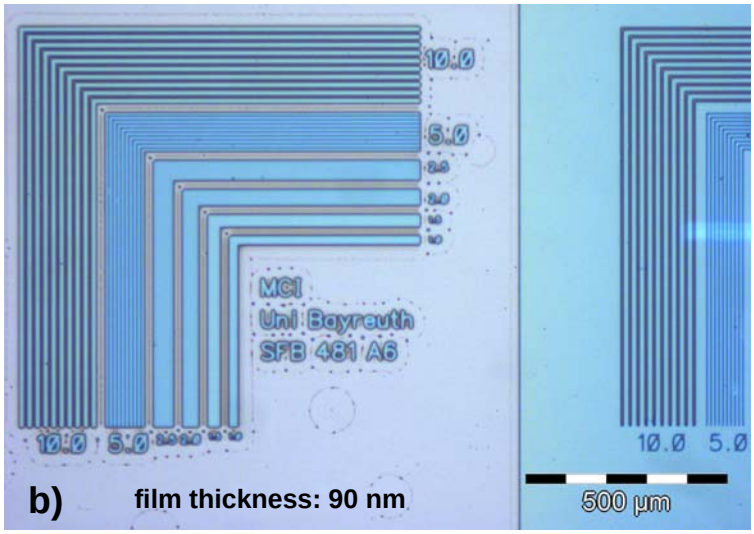
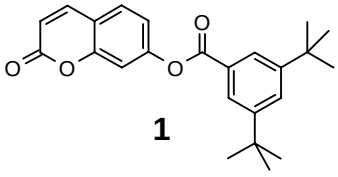


2b





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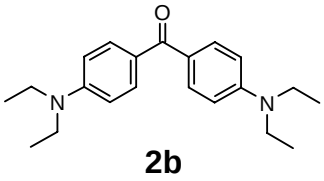

2b

Fig. 3. Reflection microscope images of patterns on a silylated Si wafer prepared by all-dry lithography (the lighter areas are the substrate surface, the darker areas consist of photoresist material). 3,5-Di-tert-butylbenzoiccoumarinester **1** and sensitizer **2b** were coevaporated in a relation of about 9:1 wt.%, exposed to 5 min and developed at 80 °C for 15 h under high vacuum. The film thicknesses are about 25 nm (3a) and 90 nm (3b), respectively. Whilst the features in the thinner film are sharp and no residues are observable, the lines in the thicker film appear softened. The film thickness seems to have a strong influence on the quality of the pattern.

In summary, we have developed an all-dry lithography process for a low-molecular negative tone photoresist. The used coumarin derivative was newly synthesized and has only one functional coumarin group. The amorphous monomer film was prepared by physical vapor deposition onto a quartz glass substrate and then exposed to UV light for defined times at different sectors of the substrate. The increasing rate of photodimerization dependent on the exposure dose was tracked by UV spectroscopy. By irradiating through a mask, patterns were produced on Si wafers. A solvent-free development could be established by thermal treatment

of the exposed substrate under high vacuum. The non-exposed monomers are evaporated whilst the photogenerated dimers in the exposed parts remain on the substrate to form patterns. The necessary exposure time could be reduced ten times by coevaporating a non-toxic sensitizer. The dimerization of the coumarin derivative and thus effectiveness of the sensitizer in dependency of the dose of irradiation was again tracked by UV spectroscopy. Since low molecular weight coumarin derivatives are self-reacting, this substance class might be an interesting approach towards smaller features in nanolithography. Additionally, the all-dry lithography is a promising way for waste reducement and the lithography accessibility of poorly soluble substances.

Experimental

Materials: All commercial chemicals were employed without further purification. 7-Hydroxycoumarin, 99%, and dimethyl aminopyridine (DMAP), 99%, were purchased from Sigma-Aldrich Co. 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDAC), 98%, was purchased from Alfa Aesar. 3,5-Di-tert-butylbenzoic acid, 99%, and 4,4'-Bis(diethylamino)benzophenone (Michler's ethyl ketone), 98%, was purchased from ABCR. Dimethyl formamide (DMF) p.A. was purchased from Acros. Technical hydrochloride acid (HCl) 31-33% was purchased from Hedinger.

3,5-Di-tert-butylbenzoiccoumarinester: At room temperature under an argon atmosphere, 7-hydroxycoumarin (3.55 g, 21.9 mmol) and DMAP (0.32 g, 2.6 mmol) were added to a stirred solution of 3,5-Di-tert-butylbenzoic acid (3.05 g, 13.0 mmol) in DMF (200 mL). After been cooled down to 0 °C, EDAC (3.0 g, 15.6 mmol) was added. The cooling was removed after 10 min and the mixture was stirred for 24 h at room temperature. The yellow solution was poured into water, and the precipitation was washed with water and diluted HCl (0.5 M) until thin layer chromatography (cyclohexane-ethyl acetate 2:1 v/v plus five drops of acetic acid as eluent) showed no spot of 7-hydroxycumarin anymore. The product was dried in a vacuum dryer at 60 °C to give 3.76 g of a white powder (76.4%). T_m 134 °C; T_g 33 °C; ^{1}H NMR (DMSO-d_6, 250 MHz): δ 8.14 ppm (d, 1H, **H**C=CHC=O), 7.96 ppm (s, 2H, 2tButyl-C-C*H*-C-C=O), 7.86 ppm (d, 1H, **H**C-CH-C-O), 7.82 ppm (s, 1H, tButyl-C-C**H**-C-tButyl), 7.48 ppm (s, 1H, C-C**H**-O), 7.36 ppm (d, 1H, HC-C**H**-C-O), 6.53 ppm (d, 1H, HC=C**H**C=O), 1.36 ppm (s, 18H, 2(C**H**$_3$)$_3$). ^{13}C NMR (DMSO-d_6, 100 MHz): 164.7, 159.8, 154.1, 153.2, 151.3, 143.9, 129.4, 128.4, 128.0, 123.8, 119.0, 116.8, 115.6, 110.5, 34.7, 31.1. Anal. Calcd. for $C_{24}H_{26}O_4$: C, 76.17; H, 6.92. Found: C, 76.11; H, 7.01. HRMS Calcd. 378.18311. Found: 378.18310.

Sample Fabrication: All fabrication steps were performed under yellow light. For UV spectra measurement, a quartz plate and for patterning, a n-type Si wafer (100) were used as substrates. Single vapor deposition as well as coevaporation was performed with Balzers PLS 500 at a pressure of 7×10^{-6} mbar. 3,5-Di-tert-butylbenzoiccoumarinester was evaporated at about 130 °C and Michler's ethyl ketone at about 115 °C. The prepared films were exposed in different sectors to defined times from 2 s to 50 min with mask aligner EVG 620 (40 mJ/cm^2 at 365 nm, spectrum of 330 to 480 nm). For subsequent UV spectra tracking, the substrate was completely exposed via a blank quartz plate. For patterning, a mask providing line widths from 1 to 10 µm was employed. The development of the exposed film was performed with a self-made small, flat vacuum chamber which was situated on a precision hot stage with one half while the other half was cooled by being placed on a brass block which was positioned in an ice bath. Typical development temperatures ranged from 55 to 120 °C, and development times in dependency of the applied temperature ranged from 1 min to 7 days.

Characterization: UV spectra before and after various exposure doses in different sectors were recorded with Analytik Jena FLASHScan 530 spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were taken on Bruker Avance 250. The developed patterns were observed with microscope Leica DMRX. Thermal characteristics were taken by Mettler TGA/SDTA851 and Perkin Elmer DSC Diamond (heating rate 10 K/min, cooling rates 10 K/min and 20 K/min).

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CONTRIBUTIONS TO CONFERENCES

Apart from the publications which are part of this thesis, I gave contributions to the following conferences.

Poster presentations

F. Pfeiffer, C. Neuber, R. Giesa, H.-W. Schmidt
"Solvent-Free Negative Photoresists based on Coumarin Derivatives"
Bayreuth Polymer Symposium (BPS), Bayreuth, Germany, 2005

F. Pfeiffer, N.M. Felix, C. Neuber, C.K. Ober, H.-W. Schmidt
"Physical Vapor Deposition of Molecular Glass Photoresists: A New Route to Chemically Amplified Patterning"
Polymers & Coatings, Mainz, Germany, 2006

ERKLÄRUNG

Hiermit erkläre ich, dass ich die vorliegende Arbeit selbstständig verfasst und keine anderen als die von mir angegebenen Quellen und Hilfsmittel verwendet habe.

Ferner erkläre ich, dass ich nicht versuche habe, anderweitig mit oder ohne Erfolg diese Dissertation einzureichen oder mich einer gleichartigen Doktorprüfung an einer anderen Hochschule zu unterziehen.

Bayreuth, Juli 2007

(Frauke Pfeiffer)